Fire Safety Aspects
of
Polymeric Materials

VOLUME 3
SMOKE AND TOXICITY
(COMBUSTION TOXICOLOGY
OF POLYMERS)

A Report by
National Materials Advisory Board
National Academy of Sciences

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of
Polymeric Materials

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Fire Safety Aspects of Polymeric Materials

a **TECHNOMIC**® publication

NOTICE

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FOREWORD

This volume is one of a series of reports on the fire safety aspects of polymeric materials. The work reported here represents the results of the first in-depth study of this important subject. The investigation was carried out by a committee of distinguished polymer and fire technology scholars appointed by the National Academy of Sciences and operating under the aegis of the National Materials Advisory Board, a unit of the Commission on Sociotechnical Systems of the National Research Council.

Polymers are a large class of materials, most new members of which are man-made. While their versatility is demonstrated daily by their rapidly burgeoning use, there is still much that is not known or not widely understood about their properties. In particular, the burning characteristics of polymers are only now being fully appreciated and the present study is a landmark in the understanding of the fire safety of these ubiquitous materials.

In the first volumes of this series the committee has identified the limits of man's knowledge of the combustibility of the growing number of polymeric materials used commercially, the nature of the by-products of that combustion, and how fire behavior in these systems may be measured and predicted. The later volumes deal with the specific applications of polymeric materials, and in all cases the committee has put forth useful recommendations as to the direction of future actions to make the use of these materials safer for society.

Harvey Brooks, Chairman
Commission on Sociotechnical Systems

ABSTRACT

This is the third volume in a series. The fire safety aspects of polymers are examined with primary emphasis on human survival. Other volumes in the series deal with materials: state of the art, test methods, specifications, and standards, fire dynamics and scenarios, aircraft (civil and military), and applications to buildings, vehicles, ships, mines and bunkers. An executive summary volume has been added to the series to pull together the disciplinary material of the first four volumes.

VOLUMES OF THIS SERIES

Volume 1	Materials: State of the Art
Volume 2	Test Methods, Specifications, Standards
Volume 3	Smoke and Toxicity
	(Combustion Toxicology of Polymers)
Volume 4	Fire Dynamics and Scenarios
Volume 5	Executive Summary
Volume 6	Aircraft — Civil and Military
Volume 7	Buildings
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PREFACE

The National Materials Advisory Board (NMAB) of the Commission on Sociotechnical Systems (CSS), National Research Council, National Academy of Sciences-National Academy of Engineering-Institute of Medicine, was asked by the Department of Defense, Office of Research and Engineering, and the National Aeronautics and Space Administration to "initiate a broad survey of fire suppressant polymeric materials for use in aeronautical and space vehicles to identify needs and opportunities, assess the state of the art in fire retardant polymers (including available materials, production, costs, data requirements, methods of test and toxicity problems), and describe a comprehensive program of research and development needed to update the technology and accelerate application where advantages will accrue in performance and economy."

In accordance with its usual practice, the NMAB convened representatives of the requesting agencies, and other agencies known to be working in the field, to determine how, in the national interest, the project might best be undertaken. It was quickly learned that wide duplication of interest exists. At the request of the other agencies, sponsorship was made available to all government departments and agencies with an interest in fire safety. Concurrently, the scope of the project was broadened to take account of the needs enunciated by the new sponsors as well as of those of the original sponsors.

The total list of sponsors of this study now comprises: Department of Agriculture, Department of Commerce (National Bureau of Standards), Department of Interior (Division of Mine Safety), Department of Housing and Urban Development, Department of Health, Education and Welfare (National Institute for Occupational Safety), Department of Transportation (Federal Aviation Administration, Consumer Product Safety Commission, Environmental Protection Agency, Postal Service, as well as the Department of Defense and National Aeronautics and Space Administration.

The committee was originally constituted on November 30, 1972. The membership was expanded to its present status on July 26, 1973. The new scope was established after presentation of reports by liaison representatives covering needs, views of problem areas, current activities, future plans, and relevant resource materials. Tutorial presentations were made at meetings held in the Academy and during site visits, when the committee or its panel met with experts and organizations concerned with fire safety aspects of polymeric materials. These site visits (upward of a dozen) were an important feature of the committee's search for authentic information. Additional inputs on foreign fire technology were supplied by the U.S. Army Foreign Science and Technology Center and the Staff Scientist.

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CONTENTS

CHAPTER 1

INTRODUCTION AND SCOPE

1.1 Scope and Methodology of the Study

The charge to the NMAB Committee on Fire Safety Aspects of Polymeric Materials was set forth in presentations made by the various sponsoring agencies. Early in its deliberations, however, the committee concluded that its original charge required some modification and expansion if the crucial issues were to be fully examined and the needs of the sponsoring organizations filled. Accordingly, it was agreed that the committee would direct its attention to the behavior of polymeric materials in a fire situation with special emphasis on human-safety considerations. Excluded from consideration were firefighting, therapy after fire-caused injury, and mechanical aspects of design not related to fire safety.

The work of the committee includes (1) a survey of the state of pertinent knowledge; (2) identification of gaps in that knowledge; (3) identification of work in progress; (4) evaluation of work as it relates to the identified gaps; (5) development of conclusions; (6) formulation of recommendations for action by appropriate public and private agencies; and (7) estimation, when appropriate, of the benefits that might accrue through implementation of the recommendations. Within this framework, functional areas were addressed as they related to specific situations, end uses were considered when fire was a design consideration and the end uses are of concern to the sponsors of the study.

Attention was given to natural and synthetic polymeric materials primarily in terms of their composition, structure, relation to processing, and geometry (i.e., film, foam, fiber, etc.), but special aspects relating to their incorporation into an end-use component or structure also were included. Test methods, specifications, definitions, and standards that deal with the foregoing were considered. Regulations, however, were dealt with only in relation to end uses.

The products of combustion, including smoke and toxic substances, were considered in terms of their effects on human safety; morbidity and mortality were treated only as a function of the materials found among the products of combustion. The question of potential exposure to fire-retardant polymers, including skin contact, in situations not including pyrolysis and combustion were addressed as deemed appropriate by the committee in relation to various end uses.

In an effort to clarify the understanding of the phenomena accompanying fire, consideration was given to the mechanics of mass and energy transfer (fire dynamics). The opportunity to develop one or more scenarios to guide thinking was provided, however, as noted above, firefighting was not considered. To assist those who might use natural or synthetic polymers in components or structures, consideration also was given to design principles and criteria.

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In organizing its work, the committee concluded that its analysis of the fire safety of polymeric materials should consider the materials themselves, the fire dynamics situation, and the large societal systems affected. This decision led to the development of a reporting structure that provides for separate treatment of the technical-functional aspects of the problem and the aspects of product end use.

Accordingly, as the committee completes segments of its work, its findings will be presented in the following five disciplinary and five end use reports:

Volume 1   Materials — State of the Art
Volume 2   Test Methods, Specifications, and Standards
Volume 3   Smoke and Toxicity
            (Combustion Toxicology of Polymers)
Volume 4   Fire Dynamics and Scenarios
Volume 5   Executive Summary
Volume 6   Aircraft (Civil and Military)
Volume 7   Residential, Non-Residential and Custodial Buildings
Volume 8   Land Transportation Vehicles
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Some of the polymer applications and characteristics are in the classified literature, and the members of the committee with security clearances believed that this information could best be handled by special meetings and addendum reports to be prepared after the basic report folumes were completed. Thus, the bulk of the output of the committee would be freely available to the public. Considering the breadth of the fire safety problem, it is believed that exclusion of classified information at this time will not materially affect the committee's conclusions.

1.2 Scope and Limitations of This Report

This volume addresses the health hazards arising as a result of the combustion and thermal decomposition of polymeric materials in fire situations. The current state of knowledge about the nature of the decomposition products involved and their harmful effects on biological systems will be reviewed. Conclusions will be discussed and recommendations made for the development of additional specific knowledge and action.

This report will not concern itself with the specific physiological reactions, therapy, and prognosis associated with body surface burns. Also, the committee has not studied or researched health hazards from uncompounded polymers. Toxicity from the usual and customary unpyrolyzed state of fire-retardant polymer formulations or components (Lee, Hebert, Sherman, Aftosmis and Waritz, 1975; Blum and Ames, 1977; Federal Register, April 8, 1977; Loewengart and Van Duuren, 1977) may sometimes outweigh fire-retardant benefits in a relatively unlikely fire situation. Environmental and toxicologic problems have been associated with flame retardants such as tris-(2,3)-dibromopropyl phosphate (Maylin, Henion, Hicks, Leibovitz, Ahrens, Gilbert and List, 1977), dichlorane (Kaiser, 1974), and polybromobiphenyl (Carter, 1976).

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1.3 Caveats

Clarity of discussion requires that positions on three equivocal issues be specified initially. Terminology associated with flammability characteristics, such as "slow-burning," self-extinguishing," and "non-combustible," is avoided because these terms have become enmeshed in ambiguity (Federal Register, July 23, 1975; Appendix B, Society of Plastics Industry, #732 3040, May 1974). These terms have been used to describe performance in certain fire tests with plastics used in building materials and low density cellular plastics used in furniture. Under actual fire conditions, these same materials have been observed to be involved in rapid flame spread, quick flashover, dense smoke production, intense heat, and the generation of toxic gases.

Data obtained from presently used small-scale laboratory tests cannot be directly extrapolated to real fire situations with their continuously varying amounts of heat, ventilation, and fuel. However, these small-scale tests may be profitably used to screen comparable candidate materials and to pinpoint toxicologically unique decomposition products. This subject is addressed in volume 2 and volume 4 of this report.

Unburned polymer systems may present a very real threat to human health and the natural environment, as indicated previously. Progress will not be achieved if the combustion toxicity hazard is simply replaced by another hazard of equal or even greater magnitude.

This volume is primarily addressed to those who need to survey the smoke and toxicity problems associated with polymeric materials involved in fires. They should not expect definitive answers but, rather, a collection of basic principles and current data to guide their own evaluation of specific situations involving the use of polymeric materials. Additionally, this volume is directed to toxicologists who wish a brief appraisal of the particular toxicity problems associated with fires but it will not attempt to present a protocol to test combustion toxicology of a polymer. This is being studied by others and is outside the charge to this committee.

1.4 Philosophy of Fire Toxicology

All chemicals are potentially capable of producing harmful effects on biological tissue. In any fire situation, it is possible to observe toxicologic effects dependent on the quantity of compounds involved, time of exposure, and the proximity of the exposed organisms to the fire. Any valid comparison of the relative health hazards from pyrolysis and/or combustion of different polymers will be based on fundamental concepts of experimental toxicology developed into a pertinent test protocol.

1.4.1 Fundamental Concepts of Experimental Toxicology

Certain general principles of toxicologic methodology have been established (Loomis, 1974; Casarett and Doull, 1975). With any given chemical:

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- A certain dose level produces *no* detectable biologic effect, but some greater level produces a significant effect on essentially all biologic systems.
- Biologic effects tend to develop only when the agent is brought into direct contact with the cells under consideration.
- Similar functions and similar metabolic pathways will tend to be similarly affected in various species.
- "Small" changes in a chemical structure *may* greatly *influence* its biologic action.

As used in the first concept, often called the concentration-response or dose-response, a dose indicates the amount of chemical administered at a specific interval of time. However, a single all-or-none dose value is of limited use in assessment of toxic potential. For example, the single result of either 100% survival tells relatively little about the lowest dose likely to be lethal and how the material under consideration compares to other materials. Preferably, comparison should be made on the basis of response at several dose levels, as shown in Figure 1, which illustrates the type of graph resulting from doses on a log scale plotted against percent mortality for two substances identified as A and B. From the graph it is clear that at dose X, both A and B, and at dose Z, B is more lethal than A. No single point would give this information.

The toxic potential by the inhalation route depends on the physical state of the chemical. Depending on the nature and size of the particles, solids and liquids as well as gases can be readily inhaled. Gases and liquids can be adsorbed on the surface of inhaled solid particles.

Combustion toxicology is inherently complex because relatively minor variations in test procedure may cause major changes in the actual dose of toxicants produced. Such procedural variations include the heat flux used, whether combustion is flaming or nonflaming, the duration of heating, physical configuration of fuel, relative mass of the material degraded, etc. Essentially, these variations represent a sampling of the basic, changing fire triangle of fuel-oxygen-heat (Emmons, 1974; Terrill, Montgomery and Reinhardt, 1977). To cite the most prevalent example, fuel burned in a hot fire with plenty of oxygen will very often yield mostly carbon dioxide, but the same fuel burned in limited oxygen may yield mostly carbon dioxide; the resultant toxicities are dramatically different.

In order that data collected at different times or by different laboratories be comparable, the methods of toxicologic testing should be precise, and the product undergoing test should be thoroughly identified. Synthetic polymers may vary due to contaminants, batch differences, changes in production technique, or intentional structural changes. Plasticizers, stabilizers and flame retardant additives are often present in appreciable proportions.

Conclusions from experimental toxicity studies need to be evaluated in terms of quantity of polymer involved in the fire, significance of observed toxicity differences, and similar important parameters.

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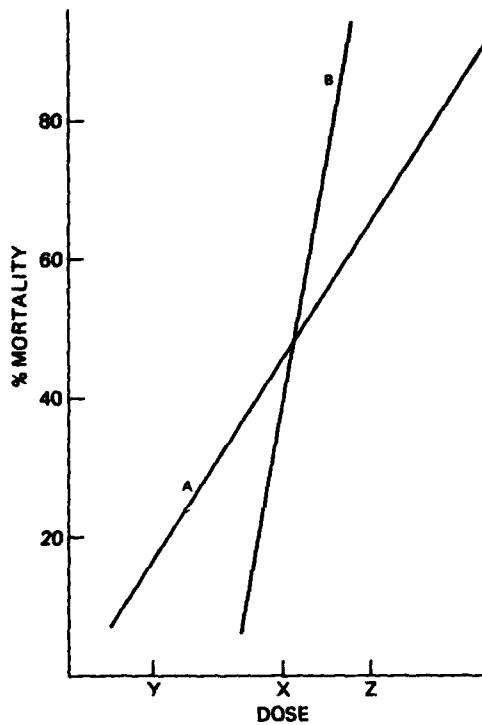
Figure 1. Effect of dose level on mortality

1.4.2 Life-Threatening Conditions Induced by Fire

Basically, the direct clinical consequences of fires stem from at least two primary sets of conditions — *elevated environmental temperatures and toxic combustion and/or pyrolysis conditions,* as shown in Figure 2. Elevated temperatures can create a stress ranging from trivial to lethal. "Toxic" combustion and/or pyrolysis conditions as discussed in Chapter 3 can be categorized as:

- Specific chemical combustion products.
- Decreased oxygen concentration.
- Smoke.*

The sum of the actual *life hazard* in fires is the interaction of at least four sets of conditions, as shown in Figure 3. To the interaction of the direct clinical consequences, we need to add both the set of variable fire conditions discussed in 1.4.1 (as mode of de-

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*In fire toxicity research a number of basic terms — particularly smoke but also combustion, pyrolysis, *inter alia* — have been used with various shades of meaning.

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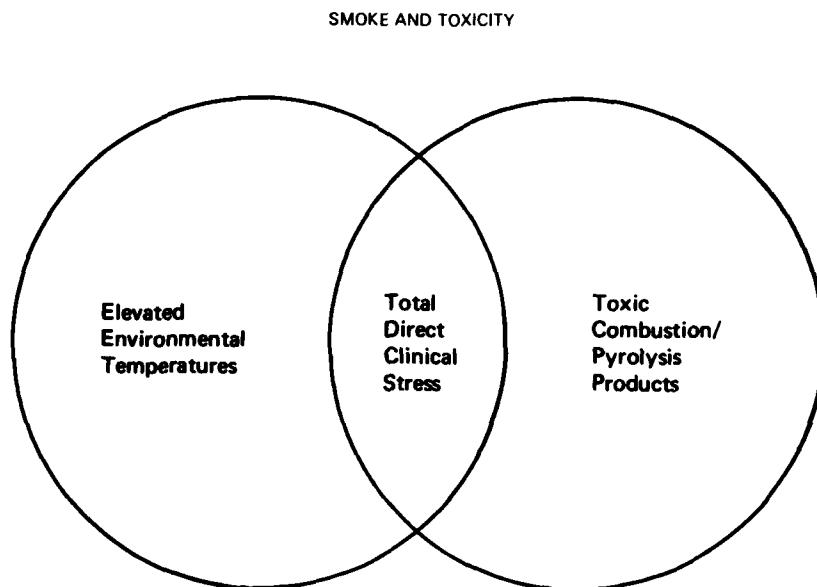
Figure 2. Direct clinical stress is produced by two primary conditions

composition, fuel and system configuration) and set of preexisting or current psychophysiological attributes. For example, preexisting heart disease has been established as a significant contributory factor in fire deaths (Radford, Pitt and Halpin, 1976). Fear, panic, or incidental trauma are recognized causes of fire death or incapacitation (Autian, 1970; Montgomery, Reinhardt, and Terrill, 1975). Assessment of the variable interaction of these four sets of conditions is obviously extremely complicated. Chapter 3 surveys the present state of the fire toxicology expertise that has risen in response to the demand for this assessment.

1.4.3 Clinical Toxicology of Products of Combustion

The hazards to human health associated with exposure to fires involving polymers can be evaluated best when epidemiologic data from humans are available to supplement animal data. Except for carbon monoxide, information concerning the clinical toxicology in humans of specific thermal decomposition products is meager. Frequently, the general subject of clinical combustion toxicology is divided into two categories, harmful effects due to smoke particles and harmful effects due to toxic gases. This division is not warranted from the toxicologic point of view, since both exposures occur simultaneously in varying degrees.

The physiologic sequence of events involved when a human death occurs during actual exposure to a fire has never been recorded. The sequence is conceptualized as the cumulative effect of a group of continuously changing variables primarily depen-

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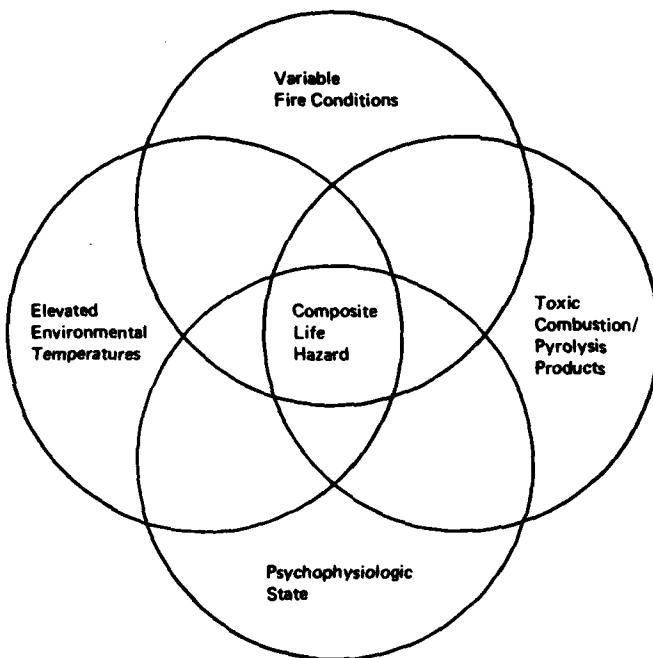
Figure 3. Composite hazard to fire victims.

dent upon the fire dynamics involved. The nature and significance of these variables, both alone and in combination, have not been completely or exhaustively investigated from the point of view of clinical toxicology. The current state of the art in regard to establishing a cause of death always involves an educated interpretation of the available pathologic and toxicologic evidence. Even in the case of fire casualties from extensively publicized conflagrations — for example, the Cocoanut Grove fire — specific data on the precise nature of the harmful role of combustion products are meager.

1.4.4 Fire Hazards

A real fire situation results in the formation of a continuously changing variety of toxicologic hazards to human health.

1.4.4.1 Hazards Common to all Fires

In the built environment, all fire situations yield:

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- *Heat.* The hazard to human health is local thermal damage (destruction of the skin and/or respiratory airway), generalized thermal shock, or some combination of local damage and generalized shock.
- *Decreased atmospheric oxygen concentration.* This factor is associated with all materials undergoing oxidation at a rapid rate such as occurs in fires. The health hazard in this situation is lack of an essential amount of available respiratory oxygen.
- *Carbon monoxide.* Any type of polymer that undergoes less than complete combustion in the presence of oxygen yields this gas. The toxicologic consequences of exposing humans to carbon monoxide have been extensively reviewed (National Academy of Sciences/NRC, Committee on Toxicology, 1973; Stewart, 1976).

As far as the amount of heat generated and the decrease in atmospheric oxygen are concerned, precisely determined physical shape and size and flammability characteristics of the end product under use conditions provide a rationale for making comparisons between polymers. However, the amount of smoke particulates and gas generated under fire conditions in a given time interval also varies as a composite function of temperature, ventilation, and fuel. (For an extended discussion of fire dynamics, see Vol. 4 in this series.) Experimental tests (Brauman, Fishman, Brolly and Chamberlain, 1976) show that fire retardant additives may, under certain circumstances, increase or vary the amount and type of smoke particulates generated for various specific reasons — elements of the retardant in the smoke, chemical effects in the gas phase due to volatile halogen from the additive, or increased mass burning rates. Similarly, fire retardant additives may influence the amount of toxic gases, such as carbon monoxide, emitted during thermal decomposition tests (Terrill, Montgomery and Reinhardt, 1977).

1.4.4.2 Hazards Related to Ventilation and Heat

In comparison to well-ventilated fires, fires that occur under poorly ventilated conditions tend to result in:

- *Significantly decreased* atmospheric oxygen.
- Limitation of the rate of combustion, thus a more *limited production* of thermal energy.
- Increased carbon monoxide and other toxic or irritant products of *incomplete combustion.*

In any real fire situation, these three categories of factors probably never exist as separate entities. Their health hazard lies in their potential for additive or synergistic interaction.

Characteristic of a well ventilated fire with adequate fuel is a constantly increasing generation of heat that, in turn, will tend to accelerate the rate of combustion. Such fires can rapidly progress to intense heat. Fire storms containing a central column of rising heated air may also have areas of significantly decreased oxygen.

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Given sufficient oxygen and thermal energy input, all organic materials will burn. Sufficient exposure of the human body to heat generated by polymer combustion will produce local or generalized burns of the surface structures and respiratory tract. The physiologic effects of burns may be significant in influencing the overall health effects of toxicologically active decomposition products.

1.4.4.3 Hazards Related to Specific Polymeric Substances

Polymers that undergo pyrolysis or combustion may yield varying amounts of heat or smoke, and/or additional specific toxicologic agents, such as hydrogen chloride, sulfur dioxide, hydrogen cyanide, and nitrogen oxides. The occurrence and quantity of these toxicants vary between various polymers and under changing fire conditions. Toxicants provide a valid basis for comparison for health safety purposes whenever two or more polymers with similar flammability characteristics are under consideration. For example, if a polymeric material undergoing combustion produces hydrogen cyanide, it may be a more hazardous material than a similar one that produce no hydrogen cyanide. However, this is true *only* when no other toxicologic factor is involved. A material which produces a small amount of hydrogen cyanide may be less of a health hazard than a compound that produces a large amount of hydrogen chloride under the same fire conditions.

Therefore, if comparative toxicologic action of the combustion products of two or more polymers to be used as a method of preferential selection, available information must include: first, the nature and amount of the toxicologic agents generated when the polymers undergo combustion or pyrolysis under specified decomposition conditions; second, the dose-response characteristics of these agents; third, the additive, antagonistic, or synergistic stress from heat or smoke generated by polymer degradation.

Nearly all polymers undergoing pyrolysis or combustion produce multiple products in continuously varying amounts. Not all of these combustion products have been toxicologically characterized. Consequently, *comparison of the health safety aspects of these combustion products can be made only* by conducting toxicologic tests with the actual polymers using experimental animals, so that the resulting data can be related to man.

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CHAPTER 2

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

2.1 Introduction

Since the first wood fires were lit, thermal degradation of polymeric materials has produced toxic products capable of exerting a variety of physiological effects. Fire may be fatal. However, surviving fire victims may carry the physical or emotional experiences of a single brief encounter with fire for years. Modern civilization recognizes that fire causes a health hazard not only for accidental victims but also for fire fighters. In most instances, exposure of fire fighters is chronic — less intense but steadily repeated.

The more serious the fire, the more the life hazard is affected by the preexisting state of health of those exposed. The outcome will be particularly affected by the general physical condition, coronary or pulmonary disease, and alcoholic or drug intoxication.

2.2 General conclusions and Recommendations

In any typical, uncontrolled fire, the toxic environment is continually changing. This environment, which actually controls the toxicity of the fire, is a function of the amount and composition of the polymers that are being degraded and the manner of decomposition which actually controls the toxicity of the fire. No condemnation can be made of synthetic polymers per se.

Present test methods are only partly adequate to evaluate polymeric materials. Also, toxic conditions generated by burning a single material may be greatly altered by the presence of other burning materials. It is erroneous to consider that simple toxicity tests offer a precise hazard evaluation. Rather, they offer a guide that may permit logical rating of toxicity under specified degradation conditions and permit the recognition of unusually toxic pyrolysis or comb ᵤstion products.

The conclusions and recommendations of this chapter represent the highest priority but other conclusions and recommendations will be found in Chapters 3 and 4.

2.3 Specific Conclusions and Recommendations

2.3.1 Analysis of Combustion Atmospheres

Conclusion: Various methodologies for the experimental study of fire toxicity are currently in use. A standard, reproducible test is needed to generate orderly ranking of experimental data that can be correlated to fire scenarios. However, the state of the art is such that it is not feasible to stipulate specific test methods in detail. *Recommendation:* Develop guidelines listing key factors for fire toxicity tests. These should serve as the basis for a future test protocol(s).

Conclusion: A given polymeric material in one use may not present the same hazard in another application. (Discussed at greater length in Volume 2 and Volume 4.) *Recommendation:* Make an attempt to evaluate the relative risk of a candidate product, based on final composition, end use, and quantity that can reasonably be anticipated in a given fire situation.

Conclusion: The chemical nature of the material being burned may or may not be particularly critical to toxicity – carbon monoxide and carbon dioxide are universal but some unusual toxicants generated by polymer combustion may be highly or even extremely toxic. *Recommendation:* Use bioassays. Chemical analysis of pyrolysis combustion products should first be used as an interpretive guide for the planning of the study of toxicity phenomena; but, chemical analysis alone is not adequate

2.3.2 Experimental Biological Effects

Conclusion: Animal and human data indicates that carbon monoxide is generally the major problem in fires. However, other toxicants, as well as particulates, may obviously be involved. *Recommendation:* Conduct further study to assess the nature and relative importance of these secondary toxicants. Evaluate smoke for obscurant properties as well as direct tissue irritation.

Conclusion: No agreement has been reached on suitable test end points. It is now recognized that mortality alone is inadequate. At present, promising incapacitation end points are sensory irritation and neuromuscular dysfunction. *Recommendation:* Expand examination and evaluation of test end points.

2.3.3 Epidemiological

Conclusion: Except with respect to carbon monoxide, data on the epidemiologic aspects of fire are too meager to compare the contribution of various factors to the fire toxicity potential as a whole. Quantitative data are particularly scarce on subjects such as amount and nature of material in a "typical room" burn, time of expoosure, effects of physical condition and general health, acute versus chronic response, and delayed effects from fires. *Recommendation:* Conduct detailed systematic studies directed to timely gathering of these types of data from fires and fire victims.

Conclusion: Increasingly, prevention of exposure to a fire environment, where feasible, is seen as the key to preventing injury. *Recommendation:* Refine and popularize early warning systems and life support systems until their use is the rule rather than the exception throughout confined areas. Design high-rise and densely populated buildings with a "fire fighting plan" emphasizing fire containment by structural design and devices such as automatic sprinklers.

CHAPTER 3

STATE OF THE ART

3.1 Introduction

In the quarter-century since a basis for the toxicology of fire was first expressed (Zapp, Jr. 1951), formal study of the life hazard from fire has progressed in two broad directions:
- Surveys of fire injuries and deaths.
- Increasingly sophisticated testing, both laboratory and large-scale.

This chapter opens with a review of basic clinical and experimental data. Next, analytical methods pertinent to current concepts of combustion toxicology are highlighted followed by an overview of experimental design.

3.2 Causes of Death and Incapacitation on Fires

Scientific study of fire fatalities began as an aftermath of the 1929 Cleveland Clinic fire. Since that time mass fatality fires and wars have enabled investigators to identify some specific causes of death and incapacitation (Birky, 1976; Montgomery, Reinhardt, Terrill, 1975; Petajan, Packham, Grunnet and Einhorn, 1975; Kimmerle, 1974; Bowes, 1974; Autian, 1970). These factors can be categorized as *thermal, chemical,* or *extrinsic* and are listed in Table 1. At any given moment in a real fire the net sum of these varying factors represents the life hazard. All the factors will be discussed, except the trauma of physical burns (See 1.1). However, the significance of body burns as an additive stress superimposed on other factors should not be overlooked.

3.2.1 Hyperthermia

Hyperthermia (abnormally high body temperature) is frequently overshadowed by other more apparent injuries and should be suspected in any case where body surface burns are more than 30%. Tests with large animals having a surface area-mass relationship near that of humans show that the relationship between exposure time and temperature is hyperbolic; Figure 1 (Moritz, Henrigues, Dutra, and Weisiger, 1947) shows that if exposure time is increased, a lower source temperature can produce a given threshold of injury. Highlights of sub- and near-lethal physiologic effects of elevated temperature are given in Figure 2 (Montgomery, Reinhardt, Terrill, 1975). In case involving a combination of respiratory dysfunction, "smoke poisoning" and cardiovascular complications, the role of hyperthermia in adding to the stress may appear less clear cut. Because, as pointed out in a recent review on heat stroke (Shibolet, Lancaster and Danon, 1976), it is difficult to determine *exactly* when body temperature is too high.

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Table 1. Nature of Fire Injuries.

Category	Comments
Thermal	Aggravated by ventilation
Direct burns	Responsible for most prolonged hospitalization
General hyperthermia or shock	A significant factor in fire fighting
Chemical	Qualitatively and quantitatively influenced by ventilation

Conditions producing hypoxia
    carbon monoxide
    hydrogen cyanide
    oxygen deficiency
	Chief cause of death, particularly carbon monoxide

Irritant gases and vapors
    sensory
    pulmonary
    general respiratory irritants
	Delay egress, cause post-exposure respiratory complications

Smoke particulate	Decreases visibility; enhances toxic effect of adsorbed gases and vapors
Miscellaneous gases and vapors	
Extrinsic	Statistics relatively scarce
Panic, emotional stress	Often difficult to determine
Accidents, falls, other trauma	
Additive strain from preexisting health conditions	Significant particularly in older persons

3.2.2 Toxic Decomposition Gases and Conditions

In any fire situation with mixed fuel, toxic combustion products are a heterogeneous mixture of gases, liquid droplets, and smoke particulates. combustion may also cause oxygen deficiency, which exerts a toxic stress and is therefore considered a toxic decomposition condition.

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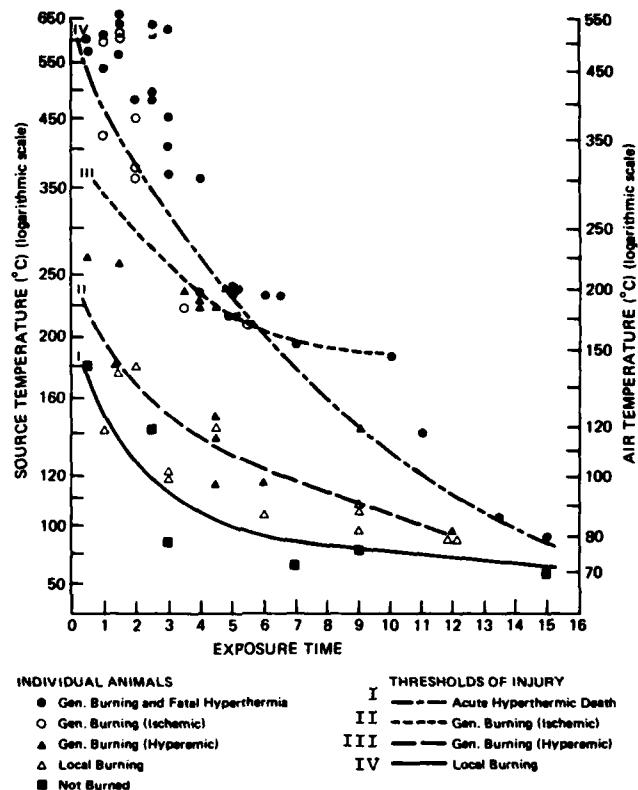
Figure 1 Effect of time elevated temperature on injury to pigs

Graph showing results of 71 experiments in which pigs had their general cutaneous surface exposed to ambient and radiant heat in an oven. Each experiment is depicted by a circle. The duration and the temperature of the exposure are indicated by the position of the circle in the grid. The effect of the exposure on the pig is shown by the character of the circle. The curved lines traversing the grid depict the approximate thresholds at which varying degrees of cutaneous and systematic injury occurred (8)

3.2.2.1 Conditions Producing Hypoxia

In fire situations, carbon monoxide (CO), hydrogen cyanide (HCN), and deficiency of oxygen (O_2) are the three most common causes of hypoxia (Brobeck, 1973 or

Figure content (temperature scale, left and right labels):

300°C — 500°F — Extremely rapid burns tolerance time strongly dependent on protective clothing

250°C

2-3 min. tolerance time with wet clothing

200°C — 400°F — Tolerance time less than 4 min. with wet skin respiratory system threshold 200°C (390°F)

Irreversible injury to dry skin in 30 sec. 180°C (360°F)

Mouth breathing difficult temp. limit for escape 150°C (300°F)

150°C — 300°F — Rapid unbearable pain to dry skin 160°C (320°F)

5 min. tolerance time 140°C (264°F)

Nasal breathing difficult 125°C (260°F) 20 min. tol. time 115°C (240°F)

15 min. tolerance time 120°C (248°F)

Very rapid skin burns in humid air 100°C (212°F)

100°C — 200°F — 25 min. tol. time 105°C (220°F)

49 min. tol. time 82°C (180°F)
Exposures above 65°C (144°F) result in central circ. failure hyperpotassemia

60 min. tol. time 70°C (158°F)

Exp. below 65°C (144°F) result in systemic hyperthermia, periph. vasc. collapse

Heat stroke 60°C (140°F)

50°C

3-5 hr. tol. time 50°C (122°F)

3-5 hr. tol. time 50°C (122°F)

100°F — Heat prostration 35°C (93°F)

Danger of heat stroke 32°C (90°F)

Heat balance cannot be maintained 30°C (86°F)

Acceptable max. for activity as anticipated in mass shelter, impos. to work efficiently 29°C (85°F)

Sleeplessness, heat rashes, limit for 14 days 27°C (80°F)

Perspiration begins, desirable max. for shelter 25°C (73°F)

0°C — 32°F — Optimum range 19-22°C (65-71°F)
Acceptable range 10-25°C (50-78°F)

Figure 2. Physiological effects of elevated temperatures on man. (3)

anoxia (Norton, 1975)*. Earlier literature regarding synergistic effects of chemicals is unclear (Armstrong, 1976), but a recent report (Sanders, Crane, Smith, Abbott and Endecott, 1975) describes a definite additive effect from CO plus HCN.

3.2.2.1.1 Carbon Monoxide (CO)

Carbon monoxide-induced hypoxia has been considered for years the major single cause of fire fatalities (Autian, 1970), but specific validating data were lacking until recently (Zikria, April, 1972; Zikria, Weston, Chodoff and Ferrer, 1972; Zikria, Budd, Floch and Ferrer, 1976; Zikria, Budd, Floch, February 1975). CO is absorbed via the

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*From a physiologic viewpoint, hypoxia is etymologically preferable (Brobeck, 1973) to anoxia, although both terms are in common use. Several types of hypoxia are recognized (Brobeck, 1973) (a) arterial hypoxia (anoxic anoxia) characterized by a lower than normal partial pressure of oxygen (PO₂) in arterial blood, (b) anemic hypoxia (anemic anoxia) characterized by a lower oxygen capacity of the blood, and (c) hypokinetic hypoxia (stagnant anoxia) characterized by a decreased rate of blood flow. Cyanide poisoning has been categorized as "histotoxic anoxia" or "cytotoxic anoxia" to describe the inability of cells to utilize the oxygen delivered (Norton, 1975), but other authors (Brobeck, 1973) prefer for this very reason to consider cyanide poisoning separate from oxygen lack per se.

lungs into the blood where because of hemoglobin's greater affinity for CO than O_2 the amount of hemoglobin (Hb) available for oxygen transport is reduced.

$$CO + HBO_2 \xrightleftharpoons{\quad K \quad} COHb + O_2$$
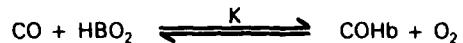
A concentration of carboxyhemoglobin (COHb) $\gtrsim$ ~ 65% results in arterial hypoxia.

Zikria and his associates have shown (Zikria, April, 1972; Zikria, Weston, Codoff and Ferrer, 1972; Zikria, Budd, Floch and Ferrer, 1976; Zikria, Budd, Floch, February 1975) that about four-fifths of "smoke poisoning" or "smoke inhalation" victims have COHb of at least a contributory level (> 10 – 15%) when admitted to the hospital. In the ongoing Johns Hopkins University fire fatality survey, now including more than 200 cases (Halpin, Fisher and Caplin, 1976; Berl and Halpin, 1976), COHb alone was sufficiently high to be the cause of death at the fire scene in 50% of the instances. In another 30% of the victims, 20 – 50% COHb was present. This significant level indicated that, overall, CO alone or CO combined with other stresses caused death in 80% of the cases studied.

3.2.2.1.2 Hydrogen Cyanide (HCN)

Fatalities in aircraft fires (Smith, 1976) and other enclosures with limited or no egress account primarily for the interest in HCN. (Lack of egress is not limited to aircraft — consider the locked jail cells in the June 1975 Seminole County, Florida, jail fire (Best, 1976).) Unfortunately, evaluation of hydrogen cyanide as an incapacitating or lethal factor is often limited by uncertainty in the cyanmide analysis. Blood cyanide levels can either fall or rise by significant amounts depending on (a) the time interval from sampling to analysis and (b) the storage technique (Curry, 1963; Ballantyne, Bright and Williams, 1974). Attribution of incapacitation and death to HCN appears very questionable in cases where egress has been prevented by mechanical means and where autopsy showed pulmonary irritation, smoke particulate in respiratory passages, and high COHb levels.

3.2.2.1.3 Oxygen Deficiency

Lowered atmospheric O_2 levels are an obvious contributory factor to hypoxia. Since the atmospheric O_2 level is generally over 17% in a pre-flashover fire, the role of decreased O_2 seems secondary to that of CO in most fires. However, gross O_2 deficiency in confined spaces has been demonstrated in experimental fires (Zapp, 1951). Symptoms of deficiency are insidious and vary with degree of deficiency, duration, and physical condition of subject (Ives, Hughes and Taylor, 1972). Generally, a 10 – 15% oxygen appears to be the critical level below which serious impairment can be expected (Ives, Hughes and Taylor, 1972; Solloman, 1957). It should be remembered that actual fires have been observed to die down as oxygen is used up and then blaze up again as

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fresh supplies enter in response to lowered pressure accompanying the cooling experienced with dying down. The oxygen concentration varies markedly at different stages of a fire but it rarely drops much below 10% of total gas concentration.

3.2.2.2 Irritant Gases and Vapors

Irritant gases and vapors produce inflammation in tissues as a result of direct contact — ordinarily, the surface tissues of the skin and mucous membranes. In fire situations, gases and vapors affecting the eyes and respiratory tract may cause tissue injury in themselves or make it difficult to see and/or breathe with the result that exit may be delayed until victims are overcome by other injuries such as CO poisoning or burns. Additionally, irritants may cause post-exposure effects that further strain an already injured respiratory tract.

Irritants have been categorized chemically (Kimmerle, 1974) or according to the characteristics of the physiological action they produce (Alarie, 1972). For the practical purposes of this review, we will consider irritants of the upper respiratory tract as sensory irritants, irritants of the lower respiratory tract as pulmonary irritants, and use a third category to describe irritants that act otherwise or by a combination of mechanisms.

3.2.2.2.1 Sensory Irritants

These chemicals inhibit respiration and cause one or more typical reflex actions associated with stimulation of trigeminal nerve endings. Such reflex actions include: burning sensation in the nose and/or in eyes, moist facial skin, sneezing, coughing, and tears (lacrimation). Typical sensory irritants are hydrogen chloride, sulfur dioxide, acrolein, and ammonia. Figure 3 (Alarie, 1972) shows a typical dose-response curve obtained by exposing mice to o-chloropbenzylidene malonitrile (CS, riot control agent).

In fire situations, one sensory irritant that has lately received increasing attention is hydrogen chloride (HCl), usually attributed to thermal decomposition from polyvinyl chloride (PVC)). The main decomposition products of polyvinyl chloride are HCl, CO, CO_2, and benzene (Boettner, 1969). However, it would appear that injurious concentrations of HC1 would probably only be inhaled in unusual circumstances, such as a fire in a vault with PVC-covered wires (Fire Journal, No. 5, 1970). Ordinarily, the strong irritant effects of HCl act as an unmistakable warning. (Speculation on the combustion of PVC has extended from the known decomposition products of HCl and CO to phosgene and chlorine (Dyer and Esch, 1976), but this is simply raising "the specter of toxicants which are not really there" (Sorensen, 1976).)

3.2.2.2.2 Pulmonary Irritants* of the Lower Respiratory Tract

These irritants typically increase respiratory rate as a result of "simulation or sensitization of various nerve endings of the lower respiratory tract" (Alarie, 1972), and such action is usually without immediate painful sensation. "True pulmonary irritants"

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*Although these irritants could be classified as sensory irritants of the lower respiratory tract on a physiologic basis, common usage of the term "sensory irritation" to refer to sensory irritation of the upper respiratory tract dictates separate terms to avoid confusion
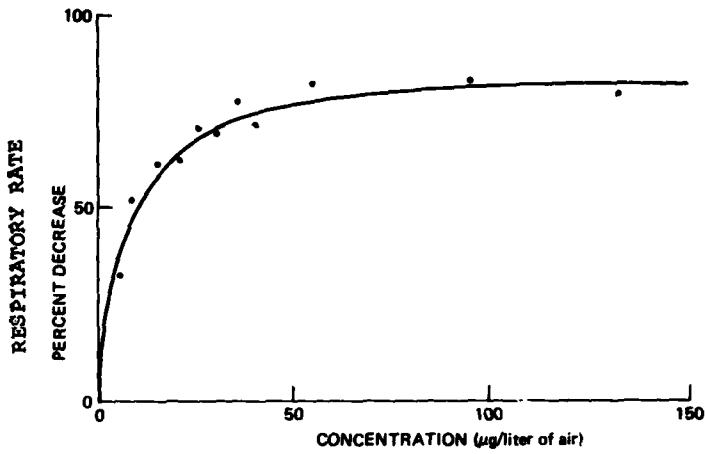
Figure 3. Effect of o-chlorobenzylidene malonitrile on the respiratory rate of mice. [26]
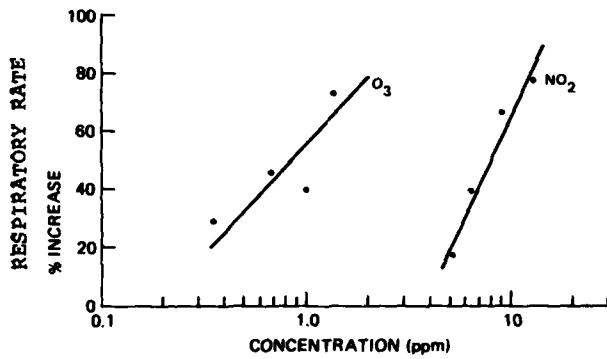
Figure 4. Effect of ozone concentration on respiratory rate on guinea pigs. [26].

are ozone, nitrogen dioxide and phosgene, since these chemicals exert their primary action solely on the lower respiratory tract. Figure 4 (Alarie, 1972) shows typical dose-response curves obtained with nitrogen dioxide and ozone.

The great majority of pulmonary irritants act as "relative pulmonary irritants"; that is, they also exert an effect as sensory irritants. (See also 3.2.2.2.3 below.)

Nitrogen oxides (NO_x), are considered the most likely pulmonary irritants in fire situations. Probably the 1929 Cleveland Clinic Fire is the only major fire associated with NO_2 as a lethal factor, but Table 2 (Fire Journal, 1974; Hillenbrand and Wray, 1974) shows that biologically significant levels of NO_x can be expected in typical residential fires. Nitrogen dioxide may cause delayed pulmonary edema (Norton, 1975), which is serious either in itself or as a contributing factor with other fire injuries.

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3.2.2.2.3 Bronchoconstrictors and General Respiratory Irritants

Bronchoconstrictors are chemicals that induce increased resistance to airflow within the conducting pathways of the ing, either by nerve stimulation on the smooth muscle airways or by liberation of histamine. (This constriction may be painful, but pain may also develop from mucosal swelling, a separate process.) Typical examples are sulfur dioxide, ammonia, and sensitizing allergens such as foreign proteins, tolylene diisocyanate, or histamine.

The term *respiratory irritant* indicates that an inhaled chemical can act as sensory irritant, pulmonary irritant, and bronchoconstrictor with little difference between the effective concentration for sensory irritation and pulmonary irritation. Typical examples are chlorine and ketene.

Table 2. Gas Concentrations in Four Experimental Fires. (31, 32).

	Danger Level Literature[a]	Typical Room[b]	Improved Room[b]	Space-Age Room[b]	Mixed-Load Room[b]
CO_2 (%)	> 8	8	3-4	1	3 (7)
O_2 (%)	< 14	12	17	20	16
CO (%)	0.1-0.2	1.5	0.5	Small	1
Hydrocarbons (ppm)		50,000	150	--	5,000
SO_2 (ppm)	50-100	100 (400)	200	Small	50 (100)
NO_x (ppm)	100-150	150 (300)	100	15	100 (200)
HCl (ppm)	1000-2000	92	260	7	22
HF (ppm)	50-250	3	0.7	0.8	0.2
HCN (ppm)	100-200	710	105	2.3	5.6
Particulate (mg/m^3)	-	5.0	3.3	0.057	0.37
Aldehydes (ppm)	-	120	1410	42	210

[a] Fire Journal article (31) refers to authors' Final Report (32) for sources of danger level estimates.

[b] "Values in parentheses indicate peak values; others are average values during first ten minutes for those measured continuously, and for the entire fire for those measured as a single integrated sample."

Sensory irritants characteristically decrease respiratory rate through action on the upper respiratory tract and pulmonary irritants increase respiratory rate through action on the lower respiratory tract; but "there is no 'counterbalancing effect' . . . It is an either-or phenomenon . . . depending on which portion of the respiratory tract is affected *first* by the lowest rate" (Alarie, 1972). Therefore, respiratory irritants that act first on the upper airways tend to decrease respiratory rate and those that act first on the lower tract tend to increase respiratory rate.

In addition to oxides of nitrogen, probably the most serious respiratory irritants in ordinary fire situations are the aldehyde gases, "which are present in wood smoke at 15 to 20 times the concentration found in kerosene smoke" (Zikria, Ferrer and Floch, 1972). Acrolein, in particular, has caused ocular and nasal irritation at concentrations as low as 3.7 ppm in animal studies (Lyon, Jenkins, Jones, Coon and Siegel, 1970). Twelve human volunteers found a 10-minute exposure to 0.8 ppm acrolein "only just tolerable for all persons concerned" (Sim and Pattle, 1957).

3.2.2.3 Smoke Particulate

In fires using mixed fuels or natural polymers, smoke particulate is a tacky, oily aggregate of carbon particles with adsorbed combustion products that are usually irritants. Massive exposure may cause direct mechanical plugging of the respiratory passages (Hart, Lee, Boyles and Batey, 1975); but, more commonly, smoke particulate is irritating to at least a minimal degree. The nature of the smoke particles generated may vary with the temperature of the fire.

Smoke particles may be small enough to be inhaled deeply into lungs. These particles can convey adsorbed irritants (Zikria, Budd, Floch, et al., 1975; Store, Haylett, Johnson and Carhart, 1973) or transfer heat (Zikria, 1972) to any part of the respiratory tract that they contact.

Smoke may also cause obscuration of vision that can result in a life hazard if exits cannot be located. Increasing recognition is being given to smoke obscuration (Robertson, May, 1975; Gaskill, 1970; Hilado, 1970; Jin, 1970; Jin, 1971; Wooley and Raftery, 1975 – 76).

In a man-made environment, a wisp or cloud of smoke particles is often the first noticeable sign of a conflagration. Even the smell of smoke can cause panic. Trauma may result as people then scramble to exits.

3.2.2.4 Miscellaneous Gases and Vapors

Miscellaneous gases and vapors may be adsorbed on the carbon smoke particles or airborne in the fire effluent. Carbon dioxide from complete oxidation of carbon atoms might be the most common product in fire situations, particularly in hot, well ventilated fires. Depending on the chemical structure of the fuel and the particular fire situation, other gases with anesthetic or drug-like properties, such as propane or benzene, may be evolved in relatively small amounts as combustion products (Ives, Hughes, and Taylor, 1972).

3.2.3 Additive and Extrinsic Stress Factors

Factors in this category are not an inherent part of fire toxicity but yet may lead to severe injury or death, either directly or by aggravation of other injuries.

3.2.3.1 Panic and Emotional Stress

Statistics are almost nonexistent. Panic, fear, or other emotional strain can result either in shock requiring direct medical attention or lead to incapacitating behavior. Lacrimation, light obscuration, and burning of the nasal passages by smoke, which is typically very irritating, all enhance the anguish of the fire victim.

3.2.3.2 Trauma

Trauma may be caused by falling objects, jumping to safety, or panic. Trauma is most likely in confined spaces such as buildings or aircraft with limited exit facilities. In a 1970 fire involving a B-747 aircraft, the fire in the engine was quickly extinguished, but 31 people were injured — most of them landing on top of one another while evacuating the aircraft by way of a chute (Fire Journal, No. 6, 1970).

3.3 Fire Fighters

A 1976 report (Balanoff, 1976) analyzing the deaths of 101 fire fighters "in-the-line-of-duty" found that 45 died from "heart attack". The average fire fighter victim dying from heart disease was 51 years old with 22 years of service. Exposure to smoke, toxic fume inhalation, stress, over-exertion, or any combinations of these were considered the main contributory causes of these "heart attack" deaths.

Fire fighters develop carboxyhemoglobin levels above that of the general population; this elevation occurs "regardless of smoking habits," according to a 6-month study of 519 Baltimore fighters (Radford and Levine, 1976). Occupational fire fighting exposure may contribute to chronic impairment of pulmonary function (Sidor and Peters, 1974; Sidor and Peters, 1974; Peters, Theriault, Fine and Wegman, 1974).

3.4 Experimentation in Fire Toxicology

Modern study dates from 1940 when Zapp and his colleagues at Edgewood Arsenal (Zapp, Jr., 1951) showed that thermal damage to the respiratory tract and chemical inhalation injury often caused fire deaths without body surface burns. Pryor and associates (Pryor, Johnson and Jackson, 1975) reported an extensive series of studies exploring the primary variables of hyperthermia, CO, anoxia, and CO_2, as well as the synergistic interaction of these variables and the superimposed effect of small amounts of hydrogen cyanide (HCN), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2). Their data indicated that anoxia and heat increased the toxicity of CO while CO_2 did not appear to increase CO toxicity. Very small amounts of HCN, NO_2, and SO_2 produced "a considerable increase in toxicity with respect to anoxia, CO and CO_2." However, some conclusions from these studies have been questioned (Montgomery, Reinhardt and Terrill, 1975; Kimmerle, 1974) and additional clarifying experiments appear desirable.

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Analytical techniques vary widely from small-scale laboratory tests to room tests. The basic approaches (Birky, 1975) that have been used in chemical analyses are: a) detailed analysis of decomposition products using gas chromatography (GC) or mass spectrometry (MS) and b) analysis for specific selected products.

Both physical and chemical characteristics of the airborne particulate influence the life hazard in fires. Depending on size, adhesiveness, and composition, smoke particles may obscure vision, physically coat the respiratory tract, and act as carrier for toxic gases (Robertson, 1974; Seader and Einhorn, 1976). Light attenuation of smoke can now be measured by specific optical density in specially designed smoke density chambers (Chien and Seader, 1974; Chien and Seader, 1975), see also cited references) or by a previously calibrated smoke-measuring transducer (Miguel and Eiger, 1976).

At present, no direct correlation between biologic, chemical, and physical characteristics of any type of fire is known. Data comparing smoke density and CO indicate that the relationship is not simple. Figures 5 and 6 (King, 1975) show the wide variations found in smoldering versus flaming exposure for five polymers tested in the National Bureau of Standards (NBS) smoke chamber.
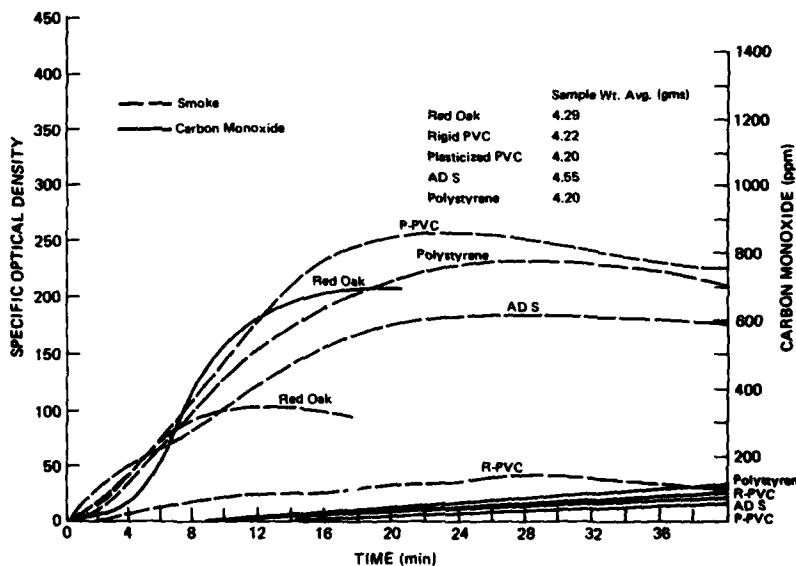
Figure 5. Smoke and carbon monoxide from various materials, average of triplicate tests smoldering exposure (2.00 w/cm²). (57)

	Sample Wt. Avg. (gms)
Red Oak	4.30
Rigid PVC	4.13
Plasticized PVC	4.10
AD S	4.42
Polystyrene	4.20
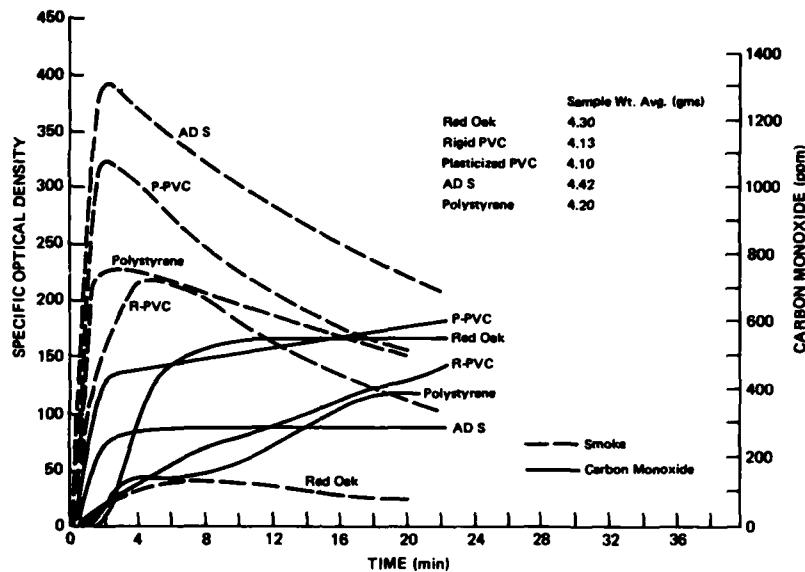
Figure 6. Smoke and carbon monoxide from various materials, average triplicate tests flaming exposure (2.00 w/cm²). (57)

3.5 Analytical Test Methodology

Sampling and analysis of thermal decomposition products are formidable tasks (Rasbash, 1967; Gaskill, 1973; Bankston, Cassanova, Powell, and Zinn, 1976; Comeford and Birky, 1972). In a few special cases — determination of hydrogen cyanide and hydrogen chloride in air — development has been initiated. In most instances, sampling and analytical methods previously developed for studies of air pollution, automotive emission, waste water, and pharmacology could be employed. These procedures have varied from extremely simple to costly and detailed.

Since measurement of individual gases only gives partial assessment or the fire's toxicity, animals — normally rats or mice — are exposed so as to get an integrated profile of toxicity. Pertinent biological determinations include blood COHb, blood cyanide, resporation rate, incapacitation, gross behavioral alterations, and death either during exposure or post-exposure. In mice or guinea pigs, respiration rate correlates well with the level of sensory irritation in the animal model.

3.5.1 Analysis of Nonabsorbing Gases and Vapors

Carbon dioxide, carbon monoxide, oxygen, and most hydrocarbons are the easiest products to sample because they are less prone to interact with particulates and water.

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Table 3. Physiologically Significant Levels for Humans of Individual Gases Given Off by Polymer Pyrolysis.

Product	General Estimate * of One-Hour Lethal Concentration (ppm)	Tentative Critical Values for Escape **
CO	4000	1500-4000
O_2	90,000 (less than)	60,000-100,000
CO_2	100,000	40,000-80,000
HCN	200-300	
HCl	1000	50-100
HBr	1000	not given (probably close to HCl)
SO_2	400-500	not given
NO_x	200-400	not given

*Value for CO from Montgomery, Reinhardt, and Terrill (3). Other values have been approximated from Henderson and Haggard, Noxious Gases and Principles of Respiration Influencing Their Action, New York, N.Y., Reinhold Publishing Co. 1943 (12).

**Values taken from Yao, Factory Mutual Research Summary Report Serial No. 22491, RC75-T-62A, Sept. 1976 (63).

Physiologically significant levels of individual gases for humans are shown in Table 3 (Henderson and Haggard, 1943; Hao, 1976). Because of the rapid rate of generation of gases in structural fires [see Figure 7 (Montgomery, Reinhardt, and Terrill, 1975; Robison, Wagner, Fristrom et. al., 1972)] and the toxicologic significance of carbon monoxide, continuous analysis methods are preferred. Optical systems such as non-dispersive infrared (NDIR) can be used for the organic analyses. Particulate and water traps are required to protect the optical systems. As an alternative, GC can be used as shown in Figure 8 (Carbosieve-B, 1976), but continuous monitoring is not possible by this method.
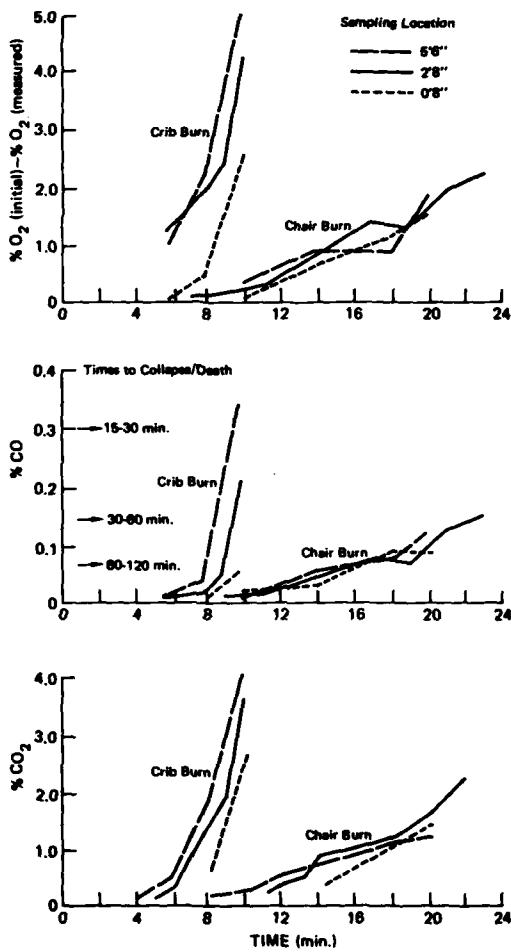
Figure 7. Gas concentration as a function of time during crib and chair burns. (3, 64)

Detailed analysis of the several hundred organic compounds that may result from pyrolysis requires high resolution GC. Peak identities are confirmed by MS analysis of the trapped or separated chromatographic effluents. Figure 9 (Einhorn, Chatfield, Mickelson and Futrell, 1974) shows separation of the organics found in pyrolysis of a heat-resistant nylon (Nomex II® — HT-4). Decomposition products often occur at *sublethal levels and then may* contribute only to sensory irritation, e.g., the effect of HCl reported to result from PVC pyrolysis (Barrow, Alarie and Stock, 1976).

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35°C to 175°C,
4 min. hold. prog.
30°C/min.

35°C to 170°C

120/140 Carbosieve-B in
9 ft. x 1/8" S.S. 50 ml/min.
Helium.

60/80 Carbosieve-B in 4 ft.
x 1/8" S.S. 40 ml/min.
Helium.
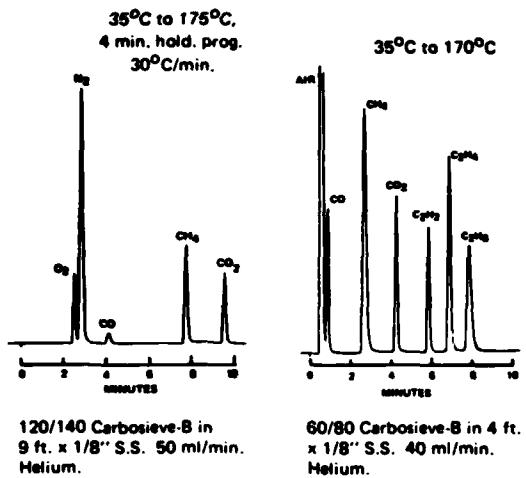
Figure 8. Typical gas chromatographic separation of CO, O_2 and CO_2 on Carbosieve-B
and separation of CO, C_1 and C_2 hydrocarbons. (65)

In an unusual case, GC/MS was used to identify a highly toxic and "atypical" pyrolysis product — 4-ethyl-1-phospha-2,6,7-trioxabicyclo(2.2.2) octane-1-oxide derived from rigid urethane foam containing trimethylolpropane plus phosphorus (Petajan, Voorhees, Packham, Baldwin, Einhorn, Grunnet, Dinger and Birky, 1975). However, based on recent publications, the widest application of these GC/MS systems has been the elucidation of polymer degradation mechanisms. Once the pathways are understood, the chemist can attempt to modify the polymer so as to block the decomposition pathway, thus theoretically improving the thermal performance of the polymer (Woolley and Fardell, March, 1976; Voorhees, Hileman, Einhorn and Futrell, 1976).

3.5.2 The Troublesome Acid Gases

HCl, HF, HCN, SO_2, and NO_x can all be absorbed by particulates, tars, and condensed water of combustion. Hence sampling these substances in the fire effluent generally requires short, heated, inert sampling lines. In most instances, continuous monitoring methods are not available. (Cyanide is an exception — see 3.5.2.2.) Moreover, no general approach such as ion specific electrodes can be used for these gases in all instances, due to interferences and lack of sensitivity.

3.5.2.1 Hydrogen Chloride (HCl)

HCl is one of the principal products from pyrolyzed or combusted polyvinyl chloride (PVC). Most investigators collect samples for HCl by scrubbing the smoke through a liquid impinger containing dilute caustic (0.1 N sodium hydroxide). The impinger sample is then analyzed for chloride using an ion specific electrode or spectrophotometric technique.
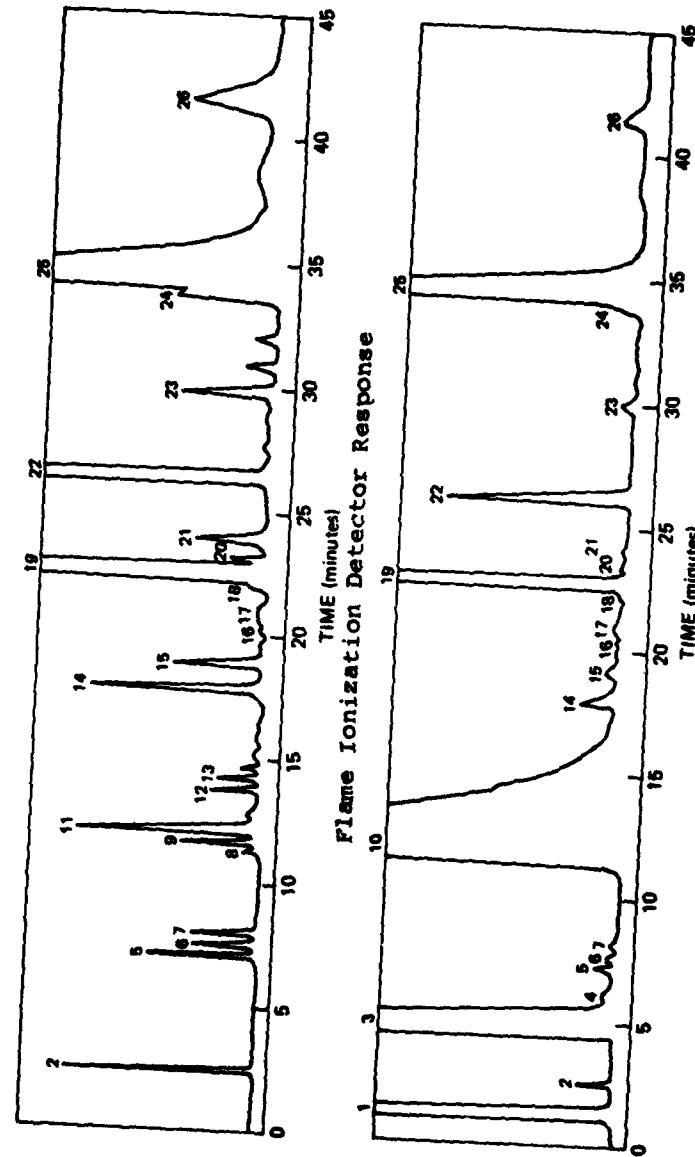
Figure 9 Volatile products from the pyrolysis of Nomex I™ fabric in nitrogen at 550°C. (66)

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Summary of the Volatile Products from the Pyrolysis of Nomex-II® Fabric in Nitrogen at 550°C[a]

Compound	Peak No.[b]	T.E.[c]	R.F.[d]	Quantity[e]
Carbon monoxide	1	0.00	0.670[f]	32.
Methane	2	0.05	1.031	2.9
Carbon dioxide	3	0.97	0.915[f]	56.
Nitrous oxide	4	1.00*	0.820[f]	0.01
Ethylene	5	0.96	0.980	0.027
Acetylene	6	0.96*	0.930	0.003
Ethane	7	0.98	1.031	0.014
Cyanogen	8	0.44*	1.5*	0.001
Propene	9	0.98*	0.652[f]	0.014
Hydrogen cyanide	11	0.44	1.5*	0.44
Water	10	0.82	0.550[f]	53.
Acetronitrile	14	0.95*	2.564	0.27
Acetone	14	0.95*	2.041	0.020
Propenenitrile	15	0.95*	1.679	0.029
Acetic acid	17	0.80*	4.167	0.43
3-Butenenitrile	18	0.95*	0.727[f]	0.17
Benzene	19	0.90	0.893	7.1
Butenenitrile	20	0.95	0.727[f]	0.020
Dioxane	21	0.95	1.25*	0.037
Toluene	22	0.95	0.935	1.9
Chlorobenzene	23	0.95*	1.10*	0.033
Xylene	23	0.95	0.971	0.13
Phenol	24	0.88	1.388	0.10
Benzonitrile	25	0.90*	1.136	13.6
Tolunitrile	26	0.90*	1.10*	1.2
Dicyanobenzene	g	0.80*	1.37*	1.1
TOTAL				170.55

*Estimated.

[a]The pyrolysis of four samples with an average weight of 56 mg of sample and a 19 mg sample weight loss during the sampling period (as measured by the TGA on the Mettler Thermoanalyzer).

[b]Corresponds to peak numbers in Figure 6 in the reference publication (66).

[c]Relative trapping efficiencies.

[d]Relative response factors for flame ionization detector.

[e]Milligrams of compound produced per gram of polymer as measured by analytical techniques.

[f]Relative response factors for the thermal conductivity detector.

[g]Elution time greater than 45 minutes, thus this peak does not appear on the chromatogram.

O'Mara has investigated the sampling of HCl in smoke extensively and demonstrated the loss of HCl due to moisture, as shown in Table 4 (O'Mara, March, 1976). Another problem in the ion specific electrode analysis is potential sulfide ion interference. Boettner and co-workers report this can be eliminated by addition of lead acetate to the impinger sample (Boettner and Hartung, 1976).

Table 4. Theoretical and Experimentally Determined Yield of Hydrogen Chloride from PVC-White Pine Smoldering Combustion.

Amount of rigid PVC: 4.12 g	
Amount of white pine: 10.65 g.	
NBS conditions: smoldering	
Theoretical yield of hydrogen chloride: 3100 ppm	
Experimental yield of hydrogen chloride if burned in the absence of wood under smoldering conditions (earlier data with PVC alone)	2350 ppm (76%)
Experimental yield of hydrogen chloride when burned in the presence of wood (and, inevitably, moisture)	1350 ppm (43%)

3.5.2.2 Hydrogen Cyanide (HCN)

HCN may be produced from any nitrogenous polymer. Also, trace amounts are reported in the combustion of cotton and paper and appear to be formed by fixation of atmospheric nitrogen. HCN gas is highly lethal and causes impairment of motor function as a result of "cytotoxic anoxia" in very low concentrations in the blood – 1/6 the lethal blood level (Sanders, Crane, Smith, Abbott and Endecott, 1975).

Sampling and analyzing HCN is difficult since this gas is absorbed or adsorbed by the moisture and smoke particles in a fire atmosphere as well as tubes and equipment. Interference is another problem. For critical work, many workers prefer impinger sampling for collecting and analyses of cyanide. A recent review discusses pros and cons of colorimetric tubes, specific ion electrodes, titrimetric methods, colorimetric method, GC, and provides a good introduction to the literature in this area (Tsuchiya and Sumi,

1976). An additional technique that combines sensitivity with relative simplicity is the bromocyanogen method with electron capture detection (Nota and Palombari, 1973); this method has been found adequate for a variety of smoke samples (Terrill, 1976).

Several continuous monitor systems are now available. Figure 10 (Tsuchiya and Sumi, 1976) shows a preliminary laboratory model designed to record the change in electric potential when HCN in a gas stream is absorbed by a flowing solution.

A Sample Gas Inlet
B Alkali Solution Inlet
C Gas and Solution Outlet
D Specific Ion Electrode
E Reference Electrode
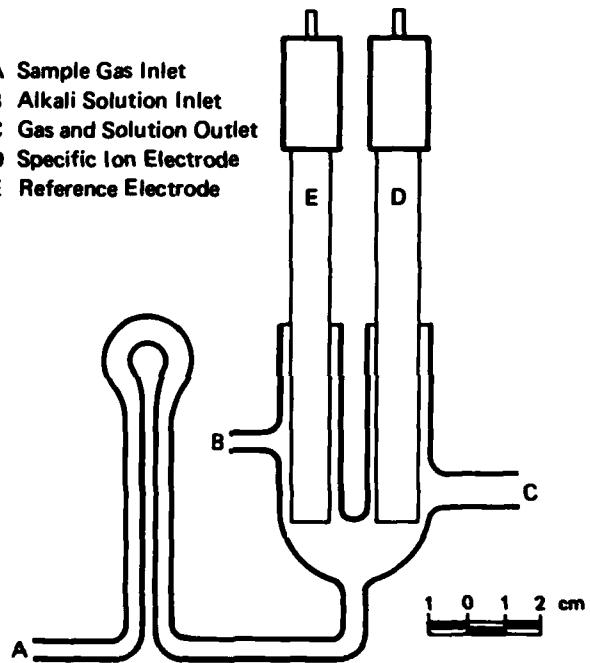
Figure 10 HCN monitoring device (73).

3.5.2.3 Hydrogen Fluoride

Hydrogen fluoride may be formed as a combustion or pryolysis product of fluorocarbon polymers. Analytical sampling systems similar to that for hydrogen chloride may be used. A fluoride ion electrode can be used to monitor impinger samples (NIOSH, 1974). Since hydrogen fluoride reacts with glass and to some degree stainless steel, these materials should be avoided in the construction of sampling systems.

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3.5.2.4 Oxides of Sulfur and Nitrogen

Several investigators have reported sulfur dioxide (SO_2) to be formed during the burning of wool. Nitrogen oxides (NO_x), as nitric oxide (NO) and nitrogen dioxide (NO_2) arise from burning a wide variety of polymers. The latter is not surprising since NO and NO_2 can be easily formed by fixation of atmospheric nitrogen at high temperatures, e.g., ca. 1600 — 1800°F. (Most NO comes from thermal decomposition.) Analytical procedures based on the chemiluminescent reaction can be used for SO_2. For NO, non-dispersive infrared analysis for continuous monitoring and Saltzman's reagent (Saltzman, 1954) for batchwise analysis are available.

3.5.3 Smoke Obscuration

All fires produce smoke, which may be thick or thin, light or dark. Any appreciable quantity invariably is irritating and obscures light and vision. A number of methods for measuring smoke obscuration have been suggested or used during the last several years (Seader and Einhorn, Aug. 1976; Chien and Seader, 1974, Chien and Seader, 1975; Miguel and Eiger, 1976). No universal or even general standard exists at present. However, in the United States, preference has been shown for the NBS smoke chamber test method.

Studies with wood, rigid urethane foam, and PVC plastic burned under non-flaming conditions show that average smoke particle sizes vary during testing, but particle sizes are generally larger for tests run at the highest levels of radiant heat (Zinn, Powell, Cassanova and Bankston, 1977)* Seader and Ou have recently proposed a theory relating optical density to particulate size and mass concentration (Seader and Ou, 1977).

Flame retardants increase carbon in the pyrolysis residue and decrease the yield of volatile aromatic products (Green, Hume and Kumar, 1976). Limited data obtained with unsaturated polyester resins suggest that formulating this type of product with maximal crosslink density and minimal aromaticity will minimize smoke generation (Miller, Petrella and Manca, 1976).

3.5.4 Biological Analyses

The easiest endpoint for biological studies of smoke is "counting dead rats or mice" (cessation of respiration). However, this gives limited information. Monitoring blood levels of the asphyxiants — CO and HCN — shows whether these agents caused, or significantly contributed to, clinical distress or death. In tests where animals survive the exposure period, they should be kept and examined daily during a recovery period. Often pulmonary edema develops during the post-exposure period. Often pulmonary

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*A new dimension has been added to smoke particle research with the elegant photomicrographs contributed by Zinn in this article

edema develops during the post-exposure period. Analysis of weight gain is a particularly helpful index for measuring overall health of the exposed animal. In practice, "biological" tests frequently use a coordinated approach, combining biological and analytical methods.

In sublethal exposures, two areas involving incapacitation of fire victims have received particular attention: neuromuscular dysfunction due to hypoxia (Norton, 1975; Courville, 1953) and intolerable sensory irritation due to the presence of compounds such as aldehydes and HCl (Alarie, 1972; Alarie, Lin and Geary, 1974).

3.5.4.1 Sensory Irritation

Reflex-induced modifications of the respiratory pattern provide a sensitive means to detect potential irritants and identify concentrations at which they will be irritating. Early investigators used a number of parameters, but Alarie and his colleagues selected respiratory rate as a simple, adequate criterion of response (Alarie, 1966). Mice are the preferred species. Guinea pigs are probably too sensitive, and rats are unsatisfactory. However, when data obtained with mice on a variety of specific compounds were compared with qualitative reports from humans (Alarie, 1972; Alarie, 1966), results showed generally good agreement. Table 5, from a 1976 paper (Barrow, Alarie and Stock, 1976), gives predicted sensory irritation responses in humans and is based on data obtained with mice exposed to the thermal decomposition products of plasticized PVC.

Thermal decomposition products of complex polymers may contain a variety of irritants, which can be identified by chemical means. Pulmonary irritants may not immediately cause obvious physiologic changes at mild to moderate levels.

3.5.4.2 Hypoxia

Neuromuscular dysfunction caused by CO and HCN has been studied in rats by failure in reflex tests (Packman, Petajan and Rens, Nov., 1973) and failure in trained activity tasks using an activity wheel (Smith, Crane, Sanders, Abbott and Endecott, 1976) or rotorod (Hartung to Terrill, 1975). Baldwin, et al., (Baldwin, Petajan and Einhorn, 1976; Petajan, Packham, Grunnet and Einhorn, 1975) emphasized investigation of the degrees of intoxication that are compatible with survival, rather than those that produce death. Three levels can be defined: a) behavioral functioning needed for escape, b) hypoxia or shock requiring immediate first-aid to avoid death; and c) moribidty following acute intoxication.

Behavioral functioning is determined by the loss of a conditioned avoidance response, which requires the normal functioning of memory as well as integration to elicit an escape response. Ischemic hypoxia or shock may suddenly reach a critical point in the course of intoxication at which point it becomes impossible to resuscitate the victim if the condition of intoxication is not reversed almost immediately. Petajan, (Petajan, Packham, Grunnet and Einhorn, 1975) considers that evaluation of effect, particularly in the central nervous system, should be based on assessment of animal function over a minimum of two weeks following exposure.

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Table 5. Prediction of Human Responses to the Thermal Decomposition Products of plasticized PVC from Sensory Irritation Data Obtained in Mice* (85).

Results Obtained in Male Swiss-Webster Mice		Predicted Sensory Irritation Responses in Humans
Exposure Concentration	$= RD_{50}$**	
Cl_2	$= 0.027$ mg/liter (9.3 ppm)	Rapidly incapacitating with
HCl	$= 0.454$ mg/liter (309 ppm)	choking and a burning sen-
PVC (first weight loss)	$= 0.19$ mg/liter	sation of the eyes, nose
PVC (second weight loss)	$= 0.13$ mg/liter	and throat
Exposure Concentration	$= 1/10$ RD_{50}	Slightly irritating but gen-
Cl_2	$= 0.003$ mg/liter (0.9 ppm)	erally tolerable with some
HCl	$= 0.045$ mg/liter (31 ppm)	stinging or burning sensa-
PVC (first weight loss)	$= 0.02$ mg/liter	tion of the eye, nose and
PVC (second weight loss)	$= 0.01$ mg/liter	throat
Exposure Concentration	$= 1/100$ RD_{50}	
Cl_2	$= 0.0003$ mg/liter (0.09 ppm)	Tolerable with very slight
HCl	$= 0.004$ mg/liter (3 ppm)	or no irritating sensation
PVC (first weight loss)	$= 0.002$ mg/liter	
PVC (second weight loss)	$= 0.001$ mg/liter	

*Results from Cl_2 and HCl are included for comparison.
**The concentration required to elicit a 50 percent decrease in respiratory rate in mice.

3.6 Experimental Design in the 1970's

In the current, rapidly evolving state of the art of combustion toxicology, any state-ment describing work in progress will be out of date from the moment pen is put to paper. At best, we can only hope to provide an introduction to recent and continuing experiments. For comprehensive coverage, "online" data bases and specialized fire research information services should be consulted.

Today experimental design for combustion toxicology involves five major concepts: fire statistics, chemical and physical analyses, biological response, a combination of chemical and biological testing, and comparative material studies. Use of the various concepts depends on test goals.

3.6.1 Fire Statistics

Fire statistics provide the direction and impetus for studies with animal models. They may also validate conclusions. For example, CO was long suspected as the main cause of fire deaths, but human studies have now demonstrated this to be so. (See 3.2.2.1.1.)

3.6.1.1 Forensic Pathology and Toxicology

Pathologic and toxicologic examinations of persons who die in fires have been customary for many years in many laboratories, but in most areas of the world, the data obtained are not generally published and hence are unavailable.

When toxicologic analytical investigation is performed, only one combustion gas, CO, has been routinely measured in the blood of fire casualties. If the blood is more than 50% saturated with CO even though the body is severely burned, it is highly probable that the person died of CO poisoning before physical burns occurred. Recently it has become increasingly clear that this gas, although ubiquitous in fire situations and not be be underrated as a cause of death, may represent only a part of the total toxicity of combustion mixtures. Consequently, some forensic laboratories now estimate blood cyanide, arising from the combustion of nitrogen-containing materials, in addition to carboxyhemoglobin saturation (Smith, Crane, Sanders, Abbott and Endecott, 1976; Caplan, 1976).

Other relationships between the fire scenario and the fate of the victims can be reconstructed quite accurately from forensic findings. In aircraft crashes accompanied by fire, a conclusion that death occurred on impact may be difficult to sustain on the basis of traumatic injury patterns alone. However, if the body is burned and there has been no absorption of CO, the judgment is confirmed. Likewise, the conlusion that non-lethal traumatic injury may have prevented escape is confirmed by high CO and/or cyanide (CN-) concentrations in a victim who is still in his original seat. High CO saturation in the absence of CN- may indicate death in proximity to burning fuel; presence of both almost certainly indicates proximity to burning aircraft interior materials.

One fundamental proviso underlies the use and usefulness of all such toxicological data – measurements must be accurate. Neither CO nor CN- is easy to measure, and it is not universally appreciated that expression of CO saturation as a percentage of available hemoglobin usually requires two measurements, each of which is subject to error.

There should be continuing efforts to improve and standardize the methods of analysis.

3.6.1.2 Clinical Investigations

In this country and abroad, a number of groups have established reputations for studies of humans who have escaped or have been rescued from fires (Levine, 1976; Zikria, Budd, Flock and Ferrer, 1976.)

Useful toxicologic information can be derived from observations on fire fighters or fire survivors who have suffered severe chemical exposure. Despite the fact that there is usually a delay between rescue and the earliest opportunity for clinical evaluation or biochemical measurements, it is frequently possible to arrive at a reasonably accurate estimate of the patient's status a the time of rescue.
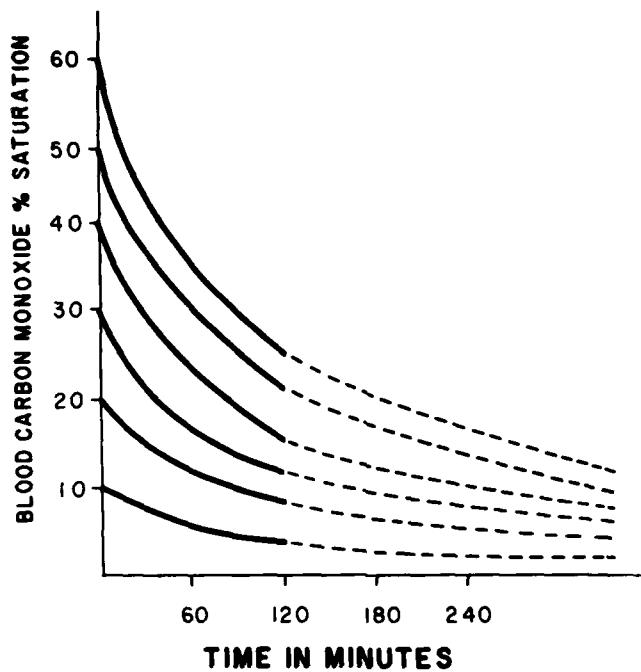
Figure 11. Clinical blood CO clearance curves (94)

Figure 11 (Zikria, Budd, Flock and Ferrer, 1976) shows clearance curves of blood COHb. Figure 12 (Zikria, Budd, Flock and Ferrer, 1976) presents clearance data in relation to several methods used for treatment.

The effects of obscuration by smoke on human behavior are complex. The optical density of an environment is quantifiable in terms of relative degrees of blindness, but the resultant impairment of escape efforts may be still an individualized matter. Effects of lacrimation, produced by gaseous/mist irritants as well as smoke particles, are difficult to assess, but they are still important to the subject in a fire environment, who may be physically unable to escape. Studies involving filtration of smoke, extraction of soluble moieties and identification of constituents may reveal more definitely the role of smoke as a toxicologic factor in the fire environment.

3.6.2 Chemical Analysis of Decomposition Products

As noted in 3.4, analyses of fire-generated toxicants have generally relied either on detailed chemical assessment of the range of thermal decomposition products or measurements of selected products. The first is highly complex due to the wide range
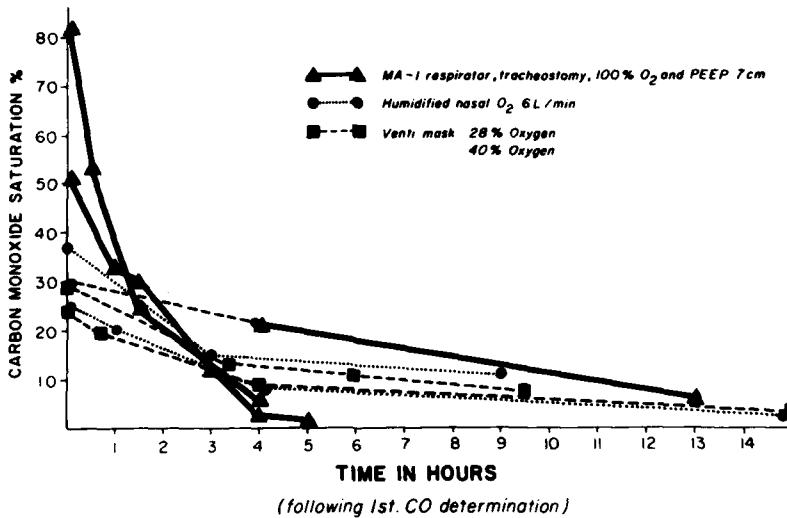
Figure 12. Carbon monoxide disappearance in blood of patients with smoke poisoning (94).

of physically different products (particulate, mist, and gas) requiring quite different methods of analysis.

The alternate approach with selected products is far simpler but in a number of cases will be based on a questionable assumption, which implies questionable significance of the resultant data. For economic reasons, measurement of selected products is the only feasible approach in many instances. In that case, the validity of the underlying assumption must be evaluated if the data are to be meaningful.

On the basis of past experience in the evaluation of the toxicology of products of combustion, it is highly improbable that a new species of highly toxic agent will be found except in those cases whereby new forms of fire retardants or dyes may be unknowingly involved in the test. If this should be so the experienced toxicologist would be alerted because of the inconsistent nature of the observed effects on the test animals. (An example is the effect of the bicyclophosphate (Petajan, Voorhees, Packahm, Baldwin, Einhorn, Grunnet, Dinger and Birky, 1975) described in 3.5.1.) Therefore it may be an unnecessary and even undesirable procedure to involve complicated chemical monitoring equipment in routine animal tests. Even with the use of GC/MS equipment there is rather minimal chance that small amounts of new, highly toxic, substances would be revealed. The most rational and economic procedure would be to reserve the elaborate techniques such as GC/MS monitoring for use when the toxicologic data demonstrate i' need.

3.6.3 Tests for Inhalation Toxicity (Biological)

Tests with experimental animals provide measurements of biological response, which fall into three main types:
- Mortality with or without accompanying clinical signs.
- Incapacitation, usually observed as loss of activity or reflex response.
- Sensory irritation.

Mortality is dramatic and relatively easy to measure*, but it is increasingly considered inadequate as the sole criterion in fire situations. More useful is a critical determination of the time of useful function (Gaume, Bartek and Rostami, 1971).

Acceptance of this viewpoint has led some investigators to regard toxic effects short of death as endpoints in animals exposed to artificial or actual combustion mixtures. Such endpoints may be collapse, coma, or earlier signs of neuromuscular dysfunction. (See 3.5.3.2.) In instrumented animals neurological, physiological or biochemical changes that indicate impending incapacitation or loss of purposeful activity could be selected. Loss of coordinated neuromuscular activity would effectively end an animal's efforts to escape from the hostile environment, and contribute to death from encroaching fire or an increasingly toxic combustion product atmosphere. By implication, the same cycle of events must happen frequently to humans trapped in fires. (Methods for observing such nonlethal effects are not new; toxicologists concerned with drug action have for many years conducted tests to determine effects on function.)

Sensory irritation (see 3.5.3.1) is, in a sense, a measure of incapacitation also. More precisely, it involves a measurement of concentration as a function of the time when reflex changes leading to incapacitation begin, not when animals are totally incapacitated. Inherently, appraisal by sensory irritation provides a measure of warning that is lacking (and has to be estimated) when mortality and/or loss of useful function are chosen as criteria.

3.6.4 Combined Analytical and Biological Testing

Most of the more recent combustion toxicology experiments conducted with animal exposures have used some chemical analyses, but the term "combined" (Birky, 1976; Montgomery, Reinhardt and Terrill, 1975) has been suggested to indicate a distinct dual approach. Such determinations may involve a number of problems, especially when particulates are present. That such an approach can be valuable is demonstrated by the comprehensive series of experiments elucidating the thermal degradation of polytetrafluoroethylene (Waritz and Kwon, 1968; Coleman, Scheel, Kupel and Larkin, 1968; Scheel, Lane and Coleman, Scheel, Kupel and Larkin, 1968; Scheel, Lane and Coleman, 1968). On a simpler scale, "combined" testing is a useful screen for appraisal of candidate polymers as shown in Table 6 (Montgomery, Reinhardt and Terrill, 1975).

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*Visual appraisal from the outside of a smoky chamber may be difficult.

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Table 6 Combustion Screen of Three Polymers (3).

Product	Chamber Atmospheres*							Mor- tality Ratio	Sample Burned wt. %
	O_2 %	CO_2 %	CO ppm	NO_x ppm	HCN ppm	HCl ppm	SO_2 ppm		
A	18.2	2.9	2330	168	868	620	–	6/6	43.0
	20.0	3.5	1150	115	660	1020	–	6/6	33.8
	18.3	4.0	1030	118	625	650	–	6/6	35 1
B	16.6	2.7	630	126	–	–	2500	1/6	41.4
	16.5	3.7	930	128	–	–	2400	3/6	41.1
	16.2	5.5	750	154	–	–	–	6/6	32.7
C	18.8	4.1	300	208	31	–	–	0/6	37.1
	18.8	4.0	350	280	34	–	–	0/6	28.7
	18.5	4.0	400	290	31	–	–	0/6	25.5

*Concentration of all gases in volume parts per million or %. In all cases, NH_3 was determined as less than 50 ppm. Dash indicates no measurement; HCN could not be determined with Product B due to sulfide and Product C contained no chlorine.

However, a rigid baseline for volume of CO production (or other stipulated decomposition product) per unit weight of candidate polymer is not practicable. In a real fire situation, intrinsic CO production from a given candidate polymer would only be significant relative to the amount of candidate polymer present. Also, in most cases, other decomposition gases would be present and CO (or any single combustion product) would be only part of the system's toxicity.

3.6.5 Comparative Material Studies

Zapp in 1962 called attention to the need for comparative material studies of natural and synthetic polymers. This is still the basic approach to evaluation of candidate synthetic polymers. But this concept must be placed in perspective. It is unrealistic to demand, for example, that all proposed building materials be "no more toxic than wood." Such a blandly dogmatic statement does not take into question how this determination shall be made nor whether the proposed material is used in comparable amounts or under equivalent conditions. The toxicity of the decomposition products of wood will vary according to different composition, different combustion conditions, and different damage mechanisms. Wood varies in composition – even samples of specific type, such as Douglas fir or white pine, are by no means chemically identical. It is also difficult to compare damage mechanisms, such as observed in lethal, gross overexposure to CO, to that observed in delayed pulmonary edema that may or not be fatal if vigorous medical treatment is administered. It is extremely difficult to define what constitutes suitable experimental combustion product exposure conditions. Available experimental data dictate caution in any proposed standardization. Several major pitfalls are identified below.

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3.6.5.1 Method of Thermal Degradation

Materials can be thermally degraded into three principal ways: anaerobic pyrolysis, oxidative pyrolysis ("smoldering"), and flaming combustion. All conditions can and probably do occur at some point, at some time, in a real fire, and they change in importance as the fire proceeds. For the purpose of toxicity evaluation, a reasonable mode or modes of combustion should be selected based on compatibility with animal testing. The majority of fires neither start nor progress anaerobically; therefore, most toxicologists consider anaerobic pyrolysis to be an unsuitable test method.

In a real fire, pyrolysis or oxidative degradation may exhibit many widely varying modes. Even when one set of test conditions is selected, comparative toxicity rankings on the same group of products can vary widely. Table 7 (Cornish, Barth and Hahn, 1976) shows the variation in "best-to-worst" toxicity ranking depending on whether a static chamber "pyrolysis" method or a dynamic chamber combustion method was used. In particular, the respective positions of the three natural polymers (red oak, cotton, and wool) in rankings obtained by the two different methods indicate that no one method provides the most severe test for a candidate synthetic polymer.

3.6.5.2 Temperature Range

Most materials, natural or synthetic, yield volatile, potentially toxic fragments at around or even below 400°C, a temperature range through which all must pass if a fire proceeds out of control. On the other hand, temperatures as high as 900°C have been recorded near ceilings in raging, large-scale test fires. For experimental screening, temperatures as low as 400°C to 500°C may be inappropriate because many polymers will not sustain their own spontaneous disintegration in this region, and the most resistant will only partially decompose. Potential toxicity cannot be tested unless the materials are forced to disintegrate completely. It is doubtful that temperatures so low could persist for long at any point in a real fire.

A temperature of 850°C may present difficulties and introduce the need for separate burning and longer transfer pathways to protect the animals from heat. For the person trapped in a fire, such high temperatures may make the prospects of survival academic unless he is far downstream from the active source.

Choosing a temperature in the vicinity of 600°C (Smith, Crane, Sanders, Abbott and Endecott, 1976; Spurgeon,) constitutes a severe test for organic materials. Many polymers decompose rapidly at this temperature. It is close to the melting point of aluminum and is the temperature at which steel glows cherry red. However, variations around this temperature may lead to significant differences. Figure 13 shows a comparison of four film samples pyrolyzed at 550°C and 650°C (Terrill, Montgomery and Reinhardt, 1977). Using the amount of CO generated as a preliminary criterion, a change in the order of preference is evident with increase in temperature from 550°C to 650°C.

Table 7. Comparative Mortality Data of Combustion Products of Polymers (99).

Static Chamber		In Order of Decreasing Toxicity		Dynamic Chamber	
LC_{50}, g	Sample	Most Toxic		Sample	LC_{50}, g
9	Red Oak	1	Wool		0.4
10	Cotton	2	Polypropylene		0.9
21	ABS (FR)	3	Polypropylene (FR)		1.2
23	SAN	4	Urethane Foam (FR)		1.3
25	Polypropylene (FR)	5	Polyvinyl Chloride		1.4
28	Polypropylene	6	Urethane Foam		1.7
31	Polystyrene	7	SAN		2.0
33	ABS	8	ABS		2.2
37	Nylon 66	9	ABS (FR)		2.3
37	Nylon 66 (FR)	10	Nylon 66		2.7
47	Urethane Foam (FR)	11	Cotton		2.7
50	Urethane Foam	12	Nylon 66 (FR)		3.2
50	Polyvinyl Chloride	13	Red Oak		3.6
60	Wool	Least Toxic	Polystyrene		6.0

With nitrogen-containing polymers, choice of degradation temperature in the vicinity of 600°C may promote formation of HCN (Spurgeon, 1975), as a result of incomplete combustion (Ball and Boettner, 1973). Faster heating rates to higher temperatures will promote complete combustion of these polymers and thus minimize cyanide formation (Ball and Boettner, 1973; Junod, 1976). This one example shows the critical influence of temperature and combustion conditions on test results.

Only one polymer, polytetrafluoroethylene, has been toxicologically characterized in various temperature ranges (Waritz and Kwon, 1968; Coleman, Scheel, Kupel and Larkin, 1968; Scheel, Lane and Coleman, 1968). Three significant temperature ranges were evident: <500°C, 500°C to 650°C, and >650°C. The major differences in the type and toxicity of the decomposition products obtained from this polymer of comparatively simple structure suggest that such analysis should be employed more extensively.

3.6.5.3 Time Frame

The total elapsed time for burning and exposure should take into consideration practical aspects. For this reason, to simulate exposure in a rapidly developing fire where the concentration of toxic substances grows very fast, it would be inappropriate to expose animals to low concentrations of toxic gases for long times. If time to incapacitation and time to death are to be observed, the toxic gas concentration should be so adjusted that incapacitation or death occurs in less than 30 minutes. Exposed animals should be observed for at least two weeks in order to detect delayed toxicity and death.
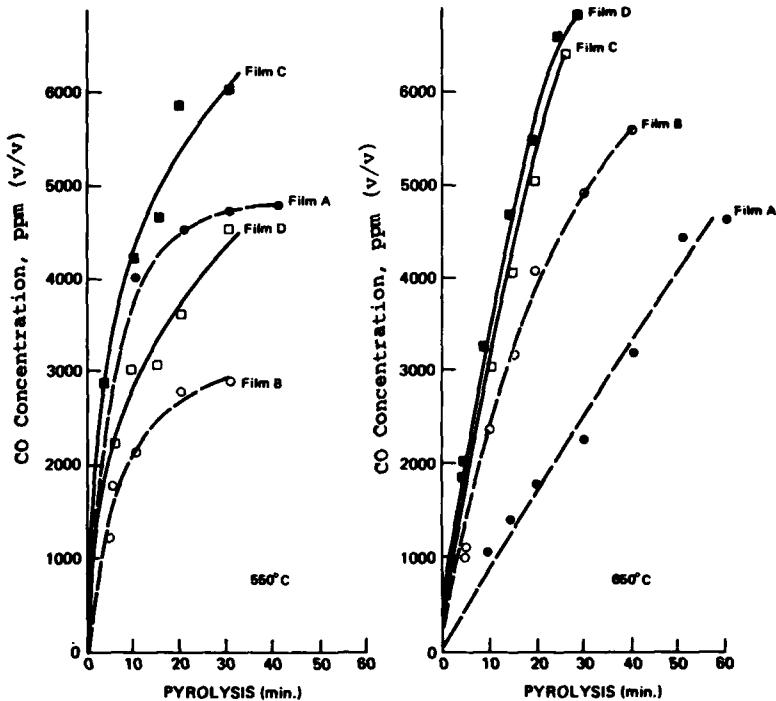
Figure 13. Generation of carbon monoxide in pyrolysis of 5_g film samples at 550"C and 650"C (102)

If animal responses are to reflect the composition of the final combustion mixture, polymer burn should be completed early in such a short exposure period, regardless of whether the temperature of burning is pre-established or programmed upward to the ignition points. The inherent resistance of a polymer to thermal decomposition will influence the rate of burning under the conditions selected, and this is an uncontrollable variable in the elapsed time to an observable toxicological reaction.

3.7 Conclusions and Recommendations

The state of the art obviously has a number of deficiencies and these are reviewed in Chapter 4, with conclusions and recommendations presented in 4.9. Several key points considered essential to the understanding and advancement of the state of the art are set forth below.

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Conclusion: Carbon monoxide is the major and most common chemical responsible for toxicity from the pyrolysis and/or combustion of polymers. Some studies involving products from specific polymers indicate a discrepancy between the quantities of CO found and mortality. *Recommendation:* In experimental studies monitor levels of CO in both the atmosphere and the blood of animals wherever practicable. In clinical studies obtain additional data regarding the role of CO as an involved toxicologic agent. In both experimental and clinical studies, the role of other possible factors should be routinely evaluated.

Conclusion: Relatively little is known about the combined biological effects (synergism) of combustion products, other than CO, that may appear during a fire. Still less is known about the time in the fire sequence when such products may reach biologically significant levels. *Recommendation:* Consider, where feasible, in research programs for studying combined effects of combustion and pyrolysis products develop before or after the more frequent problems of CO, O_2 deficiency, and excessive heat.

Conclusion: Due to the variety of methods in use in the experimental evaluation of the toxicity of pyrolysis and combustion products, as well as the failure of some of the investigators to conform to basic toxicologic principles in the design and conduct of their studies, comparison between studies is frequently impossible. *Recommendation:* Develop a standard practice for protocols for studies and reports of data so that they conform to acceptable toxicologic practice; include use of a sufficient number of animals to give statistically valid results. Make routine screening protocols uniform to the maximum extent practicable so that valid comparisons in test results can be made.

Conclusions: The experimental toxicologic studies on animals that have been conducted involve either measurement of irritant action on the airway, measurement of neuromuscular incapacitation, or measurement of lethality. At the present time, preference for any one type of measurement as the most significant for extrapolation of observed animal toxicity to man lacks adequate validation. *Recommendation:* Perform studies to evaluate the relationship between the various measurements that can be made, with the intention of resolving the question of which measurement is most appropriate.

Conclusion: Clinical investigation of the toxicity aspects of fire casualties has been conducted in only a few centers. Available data indicate that chemical (combustion product) toxicity is responsible for more incapacitation than is the physical burn phenomenon. Little or no information exists about the role of smoke obscuration in escape. *Recommendation:* Expand effort in the areas of clinical epidemiologic and toxicologic studies of fire casualties. Make funding available to centers having capability in these areas.

Conclusion: It is not possible at this time to brand a product as "good" or "bad" on the basis of isolated toxicologic tests for evaluation of polymers and their combustion products. It is feasible to provide a spectrum that reveals relative toxic potential among materials designed for the same end use. *Recommendation:* Develop and periodically update this spectrum by an appropriate, technically qualified group. Manufacturers, users, and regulatory agencies should make inputs to this group.

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CHAPTER 4

GAPS IN KNOWLEDGE OF SMOKE AND TOXICITY

4.1 Introduction

The gaps in our knowledge of the health and safety effects of smoke and toxic products from the combustion of high polymers are so numerous and ill-defined that they can only be discussed in broad categories. This chapter will give special attention to those gaps that affect current ability to predict the comparative hazards to human health among various alternative materials of construction.

4.2 Smoke and Acute Inhalation Toxicity

Smoke* may cause two kinds of hazard for persons involved in a fire. First, it reduces visibility sometimes to the point where victims cannot see exits and may be unable to escape from the fire. Second, smoke particles are irritating to the eyes and respiratory tract, probably due mostly to gases adsorbed on their surfaces. Irritation of the respiratory tract may progress from coughing and sneezing to pneumonitis and pulmonary edema.

Smoke from thermal decomposition and combustion of polymers may contain a variety of gases and mists. Many of these can be identified and studied for their effects on health and safety. To do so for each component would be a major *tour de force* and is not necessary for screening purposes, although essential for an understanding of particular problems. Most present screening methods use a fixed fuel load whereas data are needed from screening tests for several concentrations of the mixture of smoke particles and gases. This will permit the construction of a dose-response curve that can then be used in comparing test materials. A statistically valid number of animals should be exposed at each smoke concentration.

4.3 Toxicity Testing Parameters

At the present time there is no generally accepted procedure for fire and smoke toxicity screening of polymers. It is essential that such a procedure be developed promptly, standardized, and adopted. Most of the component hardware and sub-procedures are available from various fire toxicity research laboratories; it is recommended that they be amalgamated into a composite design.

Thirty minutes is probably an adequate exposure time for animal testing since relatively few real fire situations last more than 30 minutes without intolerable heat becoming the limiting factor for human survival. (Some exceptions can be found, such as fires in high-rise buildings that can result in oxygen cutoff or escape of toxic gases into the ventilating system.) To avoid undue heat stress on test animals, exposure

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*For a more detailed discussion of the effect of smoke, see 1.4.2, 3.2.2.3.

temperatures should be controlled and recorded. Animals should be observed for a minimum of 14 days after exposure to detect any residual injury in the survivors. Analytical data should be collected, as described in 4.5.

It is customary to observe the animal for signs of toxicity during and after exposure while measuring performance degradation, morbidity, and mortality. Simple procedures such as tests for incapacitation provide an estimate of the loss of ability to escape. Measurements of effect on respiratory rate may be helpful. The goal in the human exposure fire situation is to avoid mortality and irreparable injury. This, in turn, will depend on capacity to escale and/or protection from the fire environments.

4.4 Role of Chemical Analysis

In view of the importance of keeping screening tests as simple as is consistent with obtaining adequate data, elaborate analytical procedures are not recommended for screening tests. However, analyses for such "standard" gases as oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), and anticipated incapacitating gases,* for example, hydrogen cyanide (HCN) are desirable. If the mortality or morbidity observed in a screening test cannot reasonably be related to the identified gases, careful, detailed analysis of the combustion/decomposition products should then be considered.

4.5 Multiple Simultaneous Exposures

Toxicology studies generally are, and have been, almost totally concerned with single chemical compounds. Such studies reflect our regulatory practices for protecting the health of people, which with few exceptions address health questions such as: How much artificial color is safe in our food? How much lead can be in our paint? How much quartz dust is safe in the air of a foundry? It has long been recognized in real life situations, and especially in the fire scenario, that these kinds of exposures are complex with exposure to multiple toxic materials occurring simultaneously. To estimate the total body insult, some relatively crude and imprecise mathematical procedures have been developed, but these procedures are inadequate to characterize the net effect of a multiplicity of inhaled combustion products.

However, some basic understanding of the combined effects of toxic materials encountered simultaneously in fires will promote a rational design or selection of construction materials for reduced toxic effects. Components of the combustion products can interact with each other to produce a new mixture having equal, less, or more toxicity than before their interaction. These interactions may be of a chemical, physical, or biological nature. Some possible examples may illustrate this point:

(a) Both CO and HCN when tested separately are known to interfere with the utilization fo O_2 by body tissues, which suggests that their toxic effects can be additive.

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*Obviously, not all incapacitating gases can be anticipated, but previous experience (see Chapter 3) suggests, for example, that polymers containing nitrogen might yield hydrogen cyanide and/or nitrogen dioxide under fire conditions.

(b) Combustion of polymers containing sulfur might produce sulfur oxides, which are highly irritant but readily removed from an inhaled airstream by moisture in the upper respiratory tract with little damage; however, if soot or other particulate solids are present, the same sulfur oxides may be adsorbed onto their surfaces, carried deeper into the respiratory system, and produce serious effects.

(c) Both the excitement of a fire and its CO_2 level may increase respiration rate so thatmore toxic materials are inhaled in a given time.

Much research of a chemical and biochemical nature is needed in order to identify combustion products, possible interactions, and overall toxic potential in the dynamic fire exposure situation. It is known that in a fire the numerous chemicals used as fillers, stabilizers, colorants, anti-oxidants, plasticizers, cross-linkers, etc., in formulating polymer products, may interact in many and unforeseen ways. For only a very few combustion products of these additives, primarily CO, CO_2, and possibility HCN, do we know enough to be able to predict with reasonable certainty what their effects will be when inhaled for a given period of time at specified concentrations. We are ignorant of the dynamics of the physiology and toxicology of most other products of combustion, especially for the short exposure times and high concentrations characteristic of fire scenarios.

Combinations of gases must be more thoroughly investigated if a rational hazard index is to be derived for a polymeric material involved in fire. Available data indicate that the possible interaction of CO with HCN, HCl, or nitrogen dioxide (NO_2) is complex (Armstrong, 1976) and may vary as a function of time or incapacitating effect measured (Higgins, Fiorca, Thomas and Davis, 1972; Gaume, Bartek and Rostami, 1971; O'Mara, 1973; Smith, Crane, Sanders, Abbott, and Endecott, 1976). Also, many combustion products are known irritants, and some irritants may, at relatively low concentrations, cause reflex closing of the glottis or bronchospasm that can prevent oxygen from entering the lungs (Alarie, 1973). We need rapid and reliable analytical methods to study the uptake, metabolism and excretion of decomposition gases.

We know a fair amount about the entrapment, distribution and excretion of inhaled particulates as a function of their size. Inhaled, still burning combustion products of their size. Inhaled, still burning combustion products may cause local caloric burns (Zikria, 1972). We know little or nothing about such characteristics when the inhalation is rapid and by mouth rather than through the nose.

4.6 Retardants and Extinguishers

A comparatively small number of additional materials may be associated with a fire situation — intentionally. Some, the fire retardants, are added to the potential fuel in advance in order to reduce its flammability or retard its rate of combustion. Others, the extinguishants, are introduced after the fire has started in order to put it out.

Retardants can be considered as another class of materials added to fuel with problems of interaction and inherent toxic and physiologic effects. One instance of interaction has been demonstrated: if certain phosphorus compounds are used as fire retardants on urethane polymers incorporating trimethylolpropane, thermal decomposition can yield a highly toxic cyclic phosphate ester (Petajan, Voorhees, Packham, Baldwin, Einhorn, Grunnet, Dinger, and Birky, 1975). Additionally, fire retardants may, under certain circumstances, increase CO and smoke production during fires. (See 1.4.4.1 and 1.1.)

Extinguishants present a dual toxicity problem, that of the materials themselves and that of their decomposition products singly and in combination. The toxicity of extinguishants can vary widely. Nitrogen is essentially non-toxic, but it can displace a significant amount of oxygen so the atmosphere can become asphyxiating. Carbon dioxide (CO_2) in the approximate range of 1% to 10% causes a progressive increase in the rate of respiration to the point where almost all available body energy is used in the working of breathing. (The theoretical minimum extinguishing concentrations of CO_2 in air for a number of common solvents varies from 21% to 62% (National Fire Protection Association, Vol. 1, 1976) at the actual level of flames.)

Halogenated extinguishants are effective in controlling fires at various concentrations depending upon the particular extinguishant. They share with a number of organic solvents the ability to increase the susceptibility of the heart to arrhythmia and fibrillation (Reinhardt, Azar, Maxfield, Smith, Jr., and Mullin, 1971). This susceptibility is enhanced by an increase of adrenalin in the blood as normally occurs during excitement. The combination can be rapidly fatal. Each extinguishant should be evaluated for this characteristic as well as for its decomposition products.

Biologically significant levels of irritating or toxic decomposition products must be avoided. For example, the thermal decomposition of bromotrifluoromethane to hydrogen fluoride or bromide "can be minimized in properly designed systems to the point where it should be of little concern" (Ford, 1972) when controlling fires.

4.7 Interpretation of Results

Our purpose in considering the toxic effects of combustion products of polymers is to make comparative judgments of the polymers' potential for causing death, incapacitation leading to death, or permanent injury in survivors. Persons involved in fire situations may only be exposed to the toxic stress of the combustion products or may also have added stress of heat, reduced O_2 concentration, or both. Exposure to these stresses may be enhanced by confusion or reduced visibility which retard or prevent escape. It is therefore desirable that a fire toxicology test include these variables in its basic design, to the extent feasible.

Injuries in fires usually occur in a relatively brief period of time, often in a matter of seconds. Concentrations of combustion products may rapidly become overpowering. Information is needed on their rates of evolution from various polymeric systems.

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The total effect of combustion products upon the body, both in magnitude and speed of occurrence, is not merely a function of chemical concentrations to which the body is exposed. It is also a function both of the rates of various processes within the body and the body's reserve capacities. These processes include the rate of absorption into the body, which is dependent on the respiratory rate and volume; the rate of transfer to and absorption by the tissues; the rate of detoxification, metabolism, and excretion for the offending substances. We know very little about any of these dynamics of the toxicology and physiology of the components of the combustion products or of the total mixture.

The behavior of persons involved in a fire situation has often been responsible for injury. Classic stories of panic in large crowds leading to trampling and blocking of exits are but one facet of this response. Individuals may behave in an abnormal manner and become totally disoriented in otherwise familiar surroundings during a fire. During fire toxicology tests, test animals should be carefully observed for behavioral changes and any evidence of incapacitation as well as morbidity and mortality.

4.8 Coordination and Information Processing

There is an immediate need for reliable comparative information on the fire aspect of polymers to be used in the wise selection of materials for construction. Natural and synthetic polymers and formulations thereof are capable of almost infinite variation. The number of organizations becoming involved in fire tests, especially fire toxicity, is rapidly increasing. Their test methods need to be standardized so that their results can be correlated for greater understanding of the toxic hazards involved.

It seems sensible to provide some mechanism for coordinating these activities in order to avoid unnecessary duplication of effort, assure comparability of data, and focus attention on the highest priorities. A formal mandatory system would be undesirable and probably would not function well because of the diversity of interests and goals. However, a comprehensive, rapidly responsive, widely disseminated system of information exchange of past data, recent results and planned research or testing would serve these goals.

4.9 Conclusions and Recommendations

Conclusion: More research is needed on the dynamics of the physiology and toxicology of polymer combustion products. *Recommendation:* Develop a research program in each of these specific areas: (a) combined effects of irritant gases and other toxic materials produced simultaneously in fires; (b) entrapment, distribution, and excretion of particles inhaled rapidly through the mouth, as occurs in fire situations; and (c) theory and methodology for separating experimentally and recombining predictively the fire stresses of toxicity, heat, and hypoxia.

Conclusion: Tests for measuring the acute toxic effects produced by polymers in fires should be comparable among different laboratories on the basis of specific chemical and biologic indices (Protocol). *Recommendation:* Develop standard toxicity test procedures for burning conditions and exposure conditions. These procedures should include chemical analyses conducted in parallel with the animal experiments, plus measurements of the loss of capacity to escape and other behavioral effects. This is the subject of a study by the Committee on Fire Toxicology, ALS, National Research Council.

Conclusion: Guidelines on the selection of materials are necessary to minimize the fire hazard to humans in potential fire situations. These guidelines should include materials proposed for plasticizers, fillers, and fire retardants as well as the base polymer. *Recommendation:* Develop guidelines for selection of materials that take into account: (a) reactions likely to occur during combustion; (b) hazardous combustion products likelty to develop in potential fire situations; and (c) probable rate of production of smoke and gases from polymeric materials as related to the probable volume of the material in any given potential fire situation. (For example, polymers proposed as wall insulation might be a high volume use and polymers proposed as certain specialized mechanical parts might be a low volume or non-residential use.)

Conclusion: Obscurant properties of smoke have received relatively little attention. *Recommendation:* Explore any possible means of alleviating smoke obscuration. Such means should include improved selection of candidate materials and also techniques for use in potential fire situations. Techniques for dealing with obscurant effects of smoke should focus both on improved communication and pohysical dissipation of smoke through aggregation or collection of smoke particles.

Conclusion: Collecting and evaluating information on the many varied aspects of the life hazard in fire situations is difficult and is becoming increasingly more so as the complexity of combustion toxicology increases. *Recommendation:* Develop a modern, integrated information exchange to facilitate the performance of the above tasks.

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